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RUBBER CHEMISTRY AND TECHNOLOGY

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Editor.....C. C. Davis
Associate Editor.....H. L. Fisher
Secretary-Treasurer.....H. E. Simmons

Vol. IV January, 1931 No. 1

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

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Secretary-Treasurer.....H. E. SIMMONS, University of Akron, Akron, Ohio
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Sergeant-at-Arms.....E. NAHM

General Meeting in April, 1931

The meeting of the Division will be held in Indianapolis, Indiana, during the week beginning March 30. The Rubber Division meetings will be held during the forenoons of Wednesday and Thursday, April 1 and 2, with the banquet undoubtedly on Wednesday night. The headquarters of the Rubber Division will be the Severin Hotel and the headquarters of the Society will be the Claypool Hotel.

Invitation

The Rubber Division has received an invitation from the Revue Générale du Caoutchouc to participate in the International Exposition and Congress on Rubber Technology, May 15, 1931, in Paris. If anyone has material which he would like to present before such a meeting, I shall be glad to coöperate with him in getting the paper on the Paris program.

H. E. SIMMONS, *Secretary-Treasurer*

Local Group Activities

Akron Group

Oct. 27, 1930. Address by Francis E. Lloyd of McGill University on "Sources and Cultivation of Rubber."

Boston Group

Oct. 22, 1930. Addresses by J. J. Skelly of the Chas. E. Bedaux Co. on "Labor Control" and by E. B. Spear of the Vultex Corp. of America on "Some Practical Applications of Vulcanized Latex."

Chicago Group

Dec. 5, 1930. Address by H. G. Bimmerman of E. I. du Pont de Nemours & Co. on "The Manufacture of Sponge Rubber."

New York Group

Oct. 23, 1930. Address by H. G. Bimmerman of E. I. du Pont de Nemours & Co. on "Control of Uniformity of Press Cures" and by H. A. Depew of the New

Jersey Zinc Co. on "Accelerated Discoloration Tests on White Rubber Products and Methods of Measuring the Extent of the Discoloration."

Dec. 10, 1930. Address by D. A. Laird of Colgate University on "The Role of Smell in the Sales of Rubber and Methods of Deodorization," and a motion picture study of the manufacture of gas black by D. F. Cranor of Binney & Smith.

New Chairman for 1931, W. H. Whitcomb of Henry L. Scott Co. The Secretary-Treasurer is to be appointed by the new chairman and nominating committee.

Los Angeles Group

Oct. 3, 1930. Address by David Spence of the Rubber Producers on "The Production of Rubber from the Guayule Plant."

Report of the Treasurer of the Rubber Division

Bank Balance, September 4, 1930	$1208.94	
Dues and Subscriptions	373.97	$1582.91
Expenditures:		
Printing	$ 29.44	
Stamps, telegrams, etc.	23.27	
Expenses of H. E. Simmons (Cincinnati)	59.00	
Deficit at banquet	32.15	
Translations	61.80	
Stenographic services	30.00	
Payment of RUBBER CHEMISTRY AND TECHNOLOGY for October	1236.67	1472.33
Bank balance as of December 31, 1930		$ 110.58

H. E. SIMMONS, *Treasurer*

New Books and Other Publications

Rubber: An Economic and Statistical Study. By Jose Carlos de Mecedo Soares. Published by Richard R. Smith, New York City. 1930. 106 pp. $3.

The French edition of this work was published in the fall of 1928 and the original Portuguese edition still earlier, but little or no attempt has been made to bring the statistics up to date and we are still faced with "estimates" of 1929 production and consumption whose fallaciousness is now historical. The treatise remains, however, as was noted in *The Rubber Age* of November 25, 1928, "interesting as a study of the entire world rubber situation from the viewpoint of a Brazilian." One chapter discusses the rise and fall of the Stevenson Restriction Act, and another chapter, explaining the attitude of the United States on such measures, details the views of Herbert Hoover as "the principal exponent of North American opinion." After a section on the economic expansion of the United States, the author concludes that for Brazil "the order of the day must be to plant and keep on planting." The present edition was printed in Scotland and includes a short introduction by Dr. Philip Schidrowitz. [From *The Rubber Age* of New York.]

"Rubber Producing Companies—1930." Official Guide for Investors in Rubber Shares. Compiled by Mincing Lane Tea & Rubber Share Brokers' Assn., Ltd., and *The Financial Times, Ltd.*, both of London, England. Boards, 685 pages, 5¼ by 8 inches. 7s. 6d.

This annual volume is arranged on its customary plan, giving full particulars of 600 rubber companies including those with tea and coffee interests. The preface of the work reviews the 1930 situation regarding crude rubber production, consumption, and stocks. In it the opinion is advanced that if the price of rubber remains under 6 to 7d. per pound for a reasonable extended period, the greater will be the chance of consumption advancing to the level of production, with a consequent longer period of prosperity for the plantation industry. [From *India Rubber World.*]

"Rubber Information. An Industrial and Commercial Compendium." Edited by H. B. Cronshaw. Leonard Hill, Ltd., Thanet House, 231–32 Strand, London, W. C. 2, England, 1930. Cloth, 237 pages, 8½ by 10¾ inches.

This book is virtually a directory of the British rubber industry. Its scope is indicated in its full subtitle, which reads, "A Compendium of the Rubber Industry in All Its Branches, including Plantation and Factory Practice, Rubber Chemistry and Engineering, Trade Statistics, Machinery and Equipment, Rubber Chemicals and Materials, Planters and Manufacturers, Rubber Goods and Trade Marks."

In the compilation of the material contained in the volume the editor was assisted by a group of six well-known British rubber chemists and technologists, thus insuring the accuracy of the scientific data presented. The arrangement of the book is very convenient for reference, and no pains have been spared to embody in the text numerous references to recent articles on the chemistry and technology of rubber and current manufacturing practice as regards both methods and materials.

The work is to be published annually and thus will be kept abreast of new developments and record the latest information on all topics covered by the industry. [From *India Rubber World.*]

Claiming to be "a compendium of the rubber industry in all its branches," this volume is comprehensive in size and, for the most part, accurate in its contents due to the services of a group of well-known rubber men in its compilation. A

technical dictionary of about 100 pages, including many references to original papers, is followed by a list of rubber chemicals and compounding materials with important data relating to each. A statistical section includes a summary of the financial reports of plantation companies. The volume is concluded by lists of products, equipment, trade names and manufacturers, the last mentioned being unfortunately incomplete and lacking in many of the principal British manufacturing plants. [From *The Rubber Age* of New York.]

"Rubber Research Scheme (Ceylon) Second Quarterly Circular for 1930." The Ceylon Rubber Research Committee, Imperial Institute, South Kensington, London, S. W. 7, England. This circular comprises the minutes of the eighth general meeting of the Rubber Research Scheme and three reports as follows: (1) The Market Possibilities of Fractionally Coagulated Crepe. (2) Preliminary Investigation of the Effect of Different Conditions of Storage on the Hardness of Raw Rubber. (3) Sulphur Dusting as a Means of Controlling Oidium. [From *India Rubber World.*]

The United Kingdom: An Industrial, Commercial, and Financial Handbook. By Hugh Butler, *et al.* Published by the United States Department of Commerce, Washington, D. C. 1930. 975 pp. $1.75.

As an effort to survey within the compass of a single volume the highly complex economic structure of one of the leading manufacturing and trading countries of the world, which is also the largest overseas market for American goods, this handbook has been admirably prepared and should serve valuably an important purpose. A 15-page chapter on "Rubber and Rubber Products" by Robert B. Macatee reviews briefly the crude rubber industry, crude rubber marketing procedure at London, the British manufacturing industry, production costs, exports and imports, and the services performed by industrial organizations and crude rubber trade associations. Other chapters deal with the automotive products, textile and other industries, with the labor problem, production costs in general, finance, marketing, advertising, tariffs, commercial laws and living conditions. A separate section is reserved for consideration of northern Ireland. [From *The Rubber Age* of New York.]

Rubber in Aircraft Design. Published by the Rubber Growers' Association, Inc., 2 Idol Lane, Eastcheap, London, E. C. 3, England. 1930. 14 pp. For free distribution.

The applications of rubber in aircraft design are constantly being extended, as was revealed in a comprehensive series of articles in *The Rubber Age* last year. Aside from the tire equipment, a modern airplane uses an appreciable amount of rubber in shock absorbers, tension rings, mountings, upholstery, parachute design, and various accessories. This pamphlet, an illustrated reprint from the Bulletin of the Rubber Growers' Association, is a brief summary of the subject, dealing with it in general terms and omitting many of the smaller applications. [From *The Rubber Age* of New York.]

Brazilian Market for Belting. By Rudolf E. Cahn. Published by the United States Department of Commerce, Washington, D. C. 1930. $0.10.

Brazil offers a permanent and steadily increasing market for rubber and other types of belting. Belting is used in this country not only in industries but to a large extent on the farms, and the extent of the Brazilian market is indicated by the figures for agricultural and industrial production which in 1927 amounted, respec-

tively, to $900,000,000 and $850,000,000. This survey outlines the demand of the various industries of the country for belting, shows the source of supply of the country's imports and cites competitive prices for various types. [From *The Rubber Age* of New York.]

Aluminum in the Rubber Industry. Published by the British Aluminum Company, Ltd., Adelaide House, King William Street, London, E. C. 4, England. 1930. 44 pp. For free distribution.

The physical properties of aluminum make it a desirable metal for many uses in the rubber industry. Because of its lightness, strength, and resistance to corrosion, it is used in making molds for footwear, rubber gloves, and other items, for table covers, trays, mandrels, and even for latex cups, pails, and coagulating pans on rubber plantations. These uses are described in detail in this manual, which also includes a 15-page appendix on the physical properties of aluminum, its chemical reactions, and the sizes and weights of aluminum sheets and tubes. [From *The Rubber Age* of New York.]

Methods of Test Relating to Electrical Insulating Materials. Published by the American Society for Testing Materials, 1315 Spruce Street, Philadelphia, Pa. 1930. 196 pp. $1.25.

For several years Committee D-9 on Electrical Insulating Materials has been carrying on the work of the A. S. T. M. with respect to the study of tests and specifications for insulating materials, drawing up methods of testing and improving upon those now in use. The methods as drawn up in this volume give what are considered to be the best methods available at the present time. Three such standard methods and ten tentative methods of test prepared by the committee are included, together with eight specifications covering certain rubber and textile products which should be of interest in electrical testing and in particular to its practical application. [From *The Rubber Age* of New York.]

"A. S. T. M. Standards (Issued Triennially) 1930. Part II, Non-Metallic Materials." American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Cloth, 1214 pages, 6 by 9 inches. Indexed. Illustrated.

The 1930 Book of Standards is published in two parts: Part I, covering, Metals, and Part II, covering Non-Metallic Materials. The latter part contains 251 standards, of which 248 relate specifically to non-metallic materials. Of these, 14 relate to rubber products and 23 to textile materials. Both groups have special interest for rubber technologists. [From *India Rubber World.*]

A. S. T. M. Specifications and Methods of Test for Textile Materials. Published by the American Society for Testing Materials, 1315 Spruce Street, Philadelphia, Pa. 1930. 122 pp. $0.80.

Prepared by Committee D-13 on Textile Materials, this pamphlet embodies specifications covering a wide range of textile materials. It contains tolerances and test methods for cotton yarn and sewing threads, light and medium weight cotton fabrics, tire fabrics and tire cord, electrical silk and cotton tapes, asbestos yarn and tape, rayon, knit goods; tolerances for numbered cotton duck, hose and belt ducks; tire cord; methods of testing woven fabrics; specifications for testing machines, chafer tire fabrics, cement sacks, sugar bags; and definitions of terms relating to textile materials. [From *The Rubber Age* of New York.]

Cotton Fabrics and Their Uses. Published by the Textile Division, United States Department of Commerce, Washington, D. C. 1930. 48 pp. $0.05.

The result of a comprehensive survey of the different types of cotton fabrics manufactured and the uses of each fabric and of cotton in general by various industries, this report is divided into two parts. A first list gives alphabetically the names of these fabrics (approximately 200) about which information has been obtained; a second list gives under each fabric a general description thereof and its various uses; a third list gives the names of articles made in whole or in part of cotton without reference to their uses and lists the articles of cotton used by various industries and professions; and a final list gives under each use the fabrics used therefor. Uses in various branches of the rubber industry occupy an appreciable amount of space in the booklet. [From *The Rubber Age* of New York.]

Symposium on Developments in Automotive Materials. Published by the American Society for Testing Materials, 1315 Spruce Street, Philadelphia, Pa. 1930. 186 pp.

At a regional meeting in Detroit last March, the 12 papers that form this volume were originally read. The first six papers are devoted to metals, while others discuss motor fuels, automotive lubricants, automobile finishes and phenol resinoids. The one of greatest interest to the rubber industry, however, is by Walter C. Keys, chief engineer of the automotive development department of the United States Rubber Company, on "Advances in Rubber for the Automotive Industry." Mr. Keys lists 65 uses of rubber in the modern automobile and describes and illustrates many of the individual applications. [From *The Rubber Age* of New York.]

"Domestic Renewal Sales of Automobile Casings." Special Circular No. 2865. By E. G. Holt, Chief, Rubber Division, Department of Commerce, Bureau of Foreign and Domestic Commerce, Washington, D. C. Paper, 22 pp., 8 by 10½p inches, mimeographed.

This circular, dated December 10, 1930, is a comprehensive statistical study of much interest and value to manufacturers and dealers in pneumatic tires. Results and conclusions, based on an analysis of 20 years' history of tire renewal sales, are offered to aid the rubber industry in forecasting domestic renewal sales of tires in the future.

A succession of statistical tabulations worked out in accordance with the plan of analysis precede the final results compiled as "Estimated Renewal Sales per Car" and "Production of Automobile Casings by Types." From this study the author draws sundry pertinent and valuable conclusions bearing on the decline of tire renewal sales. [From *India Rubber World.*]

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The RMA Manual of Tire Repairing. Published by the Rubber Manufacturers' Association, Inc., 250 West 57th Street, New York City. 1929. 64 pp.

Tire manufacturers some years ago realized the advisability of co-operating to give the tire repairman the benefit of their combined experience and research work. In this, the third edition of this handbook published in as many years, several improvements developed by the various companies have been incorporated. The manual is being distributed to repairmen throughout the country by the Tire Accessories and Repair Materials Committee of the Association. [From *The Rubber Age* of New York.]

Chemical Engineering and Chemical Catalogue. Sixth Edition. Edited by D. M. Newitt. Published by Leonard Hill, Ltd., 231 Strand, London, W. C. 2, England. 1930. 452 pp. 15s.

Announced as a comprehensive guide to every branch of the chemical industry, this volume contains a considerable amount of valuable data and useful lists. The

chemical catalog section is said by the publisher to list practically every product manufactured in Britain, while the plant section similarly includes all machinery and equipment necessary to any production industry. Indices of manufacturers, trade names and applications are followed by a section of tables and technical data. About 1000 technical and scientific books are arranged in a bibliography under subjects and authors, and authors and titles. [From *The Rubber Age* of New York.]

Chemical Engineering Catalog. Fifteenth Edition. Published by the Chemical Catalog Company, Inc., 419 Fourth Avenue, New York City. 1930. 1168 pp. $10.

Regarded now as a standard work of reference for chemical engineers, works managers, purchasing agents, and others who buy and specify equipment and materials in chemical process industries, the Chemical Engineering Catalog in its 1930 edition is as complete and useful as ever, with even more detailed information from companies as a particular feature. This volume presents collected, condensed, and standardized catalog data of equipment, machinery laboratory supplies, heavy and fine chemicals, and raw materials. It also includes classified indices, carefully cross-referenced, and a technical and scientific book section, cataloging and briefly describing an extensive list of books in English on chemical and related subjects. [From *The Rubber Age* of New York.]

Techno-Dictionary. Compiled and published by Hubert Hermanns, Dahlemer Strasse 64A, Berlin-Lichterfelde-West, Germany. 1930. 432 pp. $3.75.

More than 8000 technical words and phrases are arranged alphabetically in this pocket dictionary in the three languages of English, German, and Italian with their equivalent in each case in the other two languages. It has been prepared especially for the readers of foreign technical periodicals, and the three sections are thumb indexed. [From *The Rubber Age* of New York.]

Annual Report of Director of Bureau of Standards. By George K. Burgess. Published by the United States Department of Commerce, Washington, D. C. 1930. 56 pp. $0.10.

Summaries of the major investigations of the Bureau of Standards in the fiscal year ended June 30, 1930, are presented in this report. Of particular interest to the rubber industry are the studies of the crystallization of rubber, abrasion tests for rubber, antioxidants in rubber compounds, and the effect of humidity and temperature on the properties of rubber compounds. [From *The Rubber Age* of New York.]

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the Oct. 10 and 20 and Nov. 10 and 20, 1930, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

Pioneers in the commercial development of rubber. JAMES C. LAWRENCE. *J. Chem. Education* **7**, 1788–1801(1930).—An historical review, with portraits of Goodyear, Marks and Oenslager. C. C. DAVIS

The trend of rubber research in the United States. ARNOLD H. SMITH. *Rev. gén. caoutchouc* **6**, No. 62, 27–32(1930).—A review and discussion. C. C. DAVIS

Isoprene and rubber. XXI. The molecular size of rubber and the nature of its colloidal solutions. H. STAUDINGER. *Kautschuk* **6**, 153–8; *Rev. gén. caoutchouc* **7**, No. 61, 4(1930); cf. *C. A.* **24**, 4655.—The structure of the rubber particle and the nature of colloidal solns. of rubber are not well understood at the present time. Most investigators (Pummerer, Myer and Mark) believe that the particles are micelles, but great differences of opinion exist regarding the size of the base mols. forming these micelles. According to Pummerer these mols. are homogeneous and have the formula $(C_5H_8)_8$, while according to Meyer and Mark they are long chains with primary valences. According to the latter the primary colloidal particles present in dil. solns. should be identical with mols. which, because of their particle size and their lability, are termed macromols. This hypothesis is confirmed by the polymeric homologous products obtained by condensation and by chem. reactions like hydrogenation. Viscosity studies at different temps. and at different concns. which are carried out with complete exclusion of O are particularly important, and by their aid it has been possible to prove that macromols. and not micelles are present in rubber solns. Moreover, viscosity studies allow the detn. of mol. wts., because as is known with semi-colloidal decompn. products, there is a relation between the sp. viscosity and the mol. wt., according to the equation: $\eta_{sp}/C = K_m M$. Besides the relative viscosity varies with the concn. for different substances according to known relations. Under these conditions it becomes possible to calc. the mol. wt. by utilizing the const. which relates concn. and the viscosity. On the basis of these detns. the mol. wt. of rubber is about 100,000, which agrees with previous osmotic measurements of Caspari and of Ostwald. This wt. corresponds very well to mol. wts. and not to micellar wts. The differences between the properties of solns. of rubber and those of low-mol. substances are explained perfectly if it is assumed that the rubber mols. have the form of long rigid threads. The field of action of such a mol. in soln. is already about 1% greater than that of an ordinary mol., and this explains why rubber does not form true solns., but forms only gel solns. The reaction of the rubber soln. does not depend therefore upon the formation of micelles but depends upon the particular state of this soln. This explains the phenomena of abnormal viscosity, osmotic pressure and swelling. Substances of low mol. wt. with a small field of action do not show these abnormal properties. It should be noted also that substances of small and of large mols. form a progressive transitional series. C. C. DAVIS

Rubber molecule or rubber micelle? H. KROEPELIN. *Kautschuk* **6**, 158–9 (1930).—This problem is of great theoretical interest since Staudinger has attempted to det. mol. wts. of high polymers by means of viscosity measurements. He assumes that only free mols. are present in dil. solns. of rubber. The problem is also of importance in explaining the phenomena of mastication, both from the point of view of changes in mol. size and from the colloidal state. Viscosity measurements alone at different temps. allow of no conclusion other than whether mols. or stable micelles are con-

cerned. From another point of view attempts have been made to answer the problem through measurements of heat of combustion of masticated rubber, but the method is not accurate enough, since with the large mol. the influence of newly formed end members is of an order of magnitude of only a few thousandths. Information can, however, be obtained through detns. of the thermal properties of rubber solns., *e. g.*, the heat of swelling and heat of diln., and these can be detd. indirectly down to concns. of 0.4%. It may be assumed that the changes found by expt. depend upon differences in the micellar structure. C. C. DAVIS

The constitution of rubber according to its swelling in liquids. P. BARY. *Rev. gén. caoutchouc* **7**, No. 62, 3–10; *Kautschuk* **6**, 121–6(1930).—An attempt was made to obtain new evidence in favor of the hypothesis that the rubber hydrocarbon in the vulcanized state consists of an intimate mixt. of different stages of polymerization where the lowest existing degree of polymerization depends on the temp. and previous history of the prepn. According to this, rubber would be made up partly of long-chain mols. and partly of short-chain ones. The miscibility of α- and β-rubber in one another requires that the substance formed by their mixt. is a solvent not only for the rubber hydrocarbon but also for many other hydrocarbons. It can now be shown that unvulcanized and vulcanized rubber behave during osmosis exactly as does a solvent toward hydrocarbons and as water does toward ammonia. The Henry law for solns. of gases applies to rubber unconditionally. The soly. of S and resins is shown by the osmotic properties of the rubber membrane. A discussion of recent work by Stamberger leads to the conclusion that the inferences which he drew from the studies of vapor pressure of jellies are wrong because there is no basis for the corresponding theories in this case. The exptl. material submitted does not justify the conclusion that rubber is a homogeneous hydrocarbon, as Harries assumed. The errors which can result from the unjustifiable comparison of 2 different phenomena are especially evident in the swelling phenomena of an individual colloid in a liquid solvent and in the satd. vapor of the same solvent, it being assumed that the temps. are the same. Investigations were carried out by B. in this connection, the results of which indicate that the vapor pressure of jellies changes with the compn. of the liquid, and it is the same as the vapor pressure of the satd. vapor for the compn. which corresponds to equil. in the vapor, less for smaller and greater for larger mixts. Expts. to prove that the vapor pressure of jellies is greater than that of the liquid were not successful. If a colloid which has been greatly swollen in a liquid is introduced into vapor its wt. changes but very slowly. The syneresis which soon commences is accompanied by the evolution of heat. The temp. of the jelly rises gradually above that of the surroundings, the vapor pressure of the exuded liquid is greater than that of the liquid in the receptacle and there one has a form of distn. Since the differences in vapor pressure depend upon variations in temp., a const. temp. is a basic condition for the detn. of vapor pressures of jellies compared to those of the swelling agent, and it is self-evident that the results are not of value. For some time it has been known that in the swelling of colloids heat is at first given off and later heat is absorbed. This leads to the assumption that the soln. of the swelling agent in rubber itself consists of 2 superposed reactions. It may then be assumed that during the increase in vol. a rupture of the mol. chains of the colloid occurs and that chem. radicals present in the liquid then attach themselves to the free affinities. Swelling then consists of 2 partial reactions, one, ordinary soln. and the other a chem. reaction, *i. e.*, a depolymerization and simultaneous solvation. The astonishing fact becomes comprehensible that a substance which swells but slowly in 2 sep. liquids not only swells greatly in a mixt. of these 2 liquids but can even be completely dispersed. If it is assumed that the swelling of rubber comprises 2 reactions, namely, diffusion of the liquid into the rubber and solvation produced by this liquid, then rubber has the properties attributed to lyophilic colloids. Expts. by Scott on the progressive swelling of rubber in liquids also lead to the conclusion that swelling is made up of 2 superposed reactions. In conclusion, a technic is described by means of which an attempt was made to det. the contraction of rubber during swelling. It was found that in toluene mixts. of a vulcanized red automobile tube, contraction was very rapid for the first minutes and reached a const. value after 2 or 3 hrs. With pale crepe in CCl_4, a very sharp rise in contraction was also observed at the beginning and finally a const. end point was reached. By means of these measurements it was proved that contraction, which corresponds to the exothermic part of the swelling, is not accompanied by any corresponding effect in the endothermic part, which is indicated by an increase in vol. Therefore, only if the heat which appears during the first part of the swelling is due to phys. causes would the cooling during further swelling or soln. originate in some other way. Probably it can be traced to the chem. phenomenon of solvation. C. C. DAVIS

Rubber as a raw material in electrical engineering. H. HEERING. *Kautschuk* 6, 129–36; *Rev. gén. caoutchouc* 7, No. 62, 17–25(1930).—The importance of an insulating material from the elec. point of view depends upon the following 4 properties: (1) insulating resistance, (2) dielectric const., (3) efficiency factor and (4) resistance to puncture. Rubber has such a high elec. resistance that it can for the most part be considered as a nonconductor. The addn. of S to rubber for vulcanization increases the insulating property and, what is still more important from the elec. point of view, also increases its resistance to penetration by moisture. As far as the action of fillers in mixts. of rubber is concerned from the point of view of their insulating properties, this action depends very much on the behavior of these fillers toward water. The addn. of a small quantity of lampblack affects but slightly the insulating properties of rubber, but if a large quantity is added the insulating properties can be considerably reduced. The dielec. const. is of great practical importance; for low-current cables the capacity depends on the dielec. const. of the insulating cover, while for high-intensity currents the dielec. const. is equally important because of its influence on the distribution of the elec. field. The phenomena produced in a dielectric under the influence of a large elec. field, which depend not only on the dielec. const. but equally on the efficiency factor, can be explained by the application of the Debye theory. According to this theory, the elec. field acting from without exerts a deforming action on the field of force of the mol. The dielec. const. is influenced by this interior tension. With a. c. the direction of the size of the elec. field varies continuously, causing a corresponding deformation of the mol., a process which is transformed into heat because of internal friction of the substance, and which like the efficiency factor results in the well-known loss of a. c. If the intensity of the elec. field exceeds a certain characteristic value for each dielectric, the intensity which causes puncture is reached, the dielectric is punctured and a breakdown of the elec. field results from the local destruction of the insulating substance. The resistance to puncture is a very important factor in the safe operation of high-current installations. Unfortunately very great difficulties prevent the precise detn. of this very important const. By placing electrodes in a semi-conducting liquid (in the present expts. a soln. of castor oil in alc. was used) some of the difficulties which have been encountered in the past in the detn. of this const. are overcome. Puncture tests were carried out on sheets 1 mm. thick on the following products: (1) smoked sheet; (2) pale crepe; (3) a mixt. of smoked sheet 100, S 3, stearic acid 3, ZnO 10, mercaptobenzothiazole 1 in 4 conditions: (*a*) unvulcanized slab; (*b*) vulcanized under pressure; (*c*) vulcanized in steam; and (*d*) vulcanized in hot air; (4) base mix 3, American gas black 30; (5) base mix 3, German black 30; and (6) base mix 3, inactive black 30. A table is included showing graphically the av. values of resistance to puncture, which were: 17.5, 16.0, 15, 21, 10, 17, 1.7, 5.2 and 15 kv. per sq. mm., resp., for mixts. 1 to 6. C. C. DAVIS

Application of the falling cylinder to the measurement of the viscosity of thick rubber cements. W. F. BUSSE AND W. B. DOGGETT. *Ind. Eng. Chem., Anal. Ed.* 2, 314–9 (1930).—It is shown on a theoretical and exptl. basis that the time of fall t of cylinders through many thick cements can be represented with reasonable precision by the equation: $dt = kdx^2/(W - \pi r^2 \rho x)^n$, or integrated form: $t = k(x^2/W^n)\{1 + (2n/3)(\pi r^2 \rho x/W) + [2n(n+1)/(4 \times 2!)](\pi r^2 \rho x/W)^2 + [2n(n+1)(n+2)]/(5 \times 3!)](\pi r^2 \rho x/W)^3 + \ldots\ldots\}$, where ρ is the d. of the cement, n is a const. of the cement and k is a const. independent of the distance of fall, of x and of the wt. W, but does vary with the cement and the diam. of the cylinder. This equation was tested with cylinders of 0.0487 – 1.32 cm. diam. in liquids with viscosities from that of castor oil (6.5 poises, giving $k = 0.007$) to that of a pigmented rubber mixt. which gave $k = 0.90$, with a cylinder of 0.122 cm. diam. In contrast to rubber solns., an oil suspension of clay (15%) had a definite yield value and an anomalous turbulence. Falling-cylinder viscometers were designed for control testing, and simplified equations were derived. These were satisfactory for cements with viscosities from that of U. S. Standard Oil No. 7 ($k = 0.0486$) to cements with k 50 times as much and n values up to about 1.5. Cements of slightly masticated rubber did not follow the law upon which the equations are based, so the falling-cylinder viscometer did not give consistent n and k values. Even in these cases, however, the viscometers can be used for control testing, provided that the shearing force at the surface of the cylinder is not greater than the adhesion of the cement to cylinder surface. The viscometers have been used in testing asphalts with viscosities up to about 900,000 poises. Readings are easily made at several shearing stresses, and the viscometers should be useful with other substances, including opaque and transparent liquids with a wide range of flowing properties. C. C. D.

The viscosity of rubber solutions under the influence of benzoyl peroxide. G. FROMANDI. *Rev. gén. caoutchouc* 7, No. 64; *Gummi-Ztg.* 44, 2029(1930).—The detn.

of fillers in rubber mixts. offers difficulties because their disintegration in paraffin oil often gives products which cannot be filtered without centrifuging. Expts. show that filtration without resort to centrifuging is easy if the sample is dissolved in boiling decalin (decahydronaphthalene), which requires about 4–8 hrs. and is then heated another 1–2 hrs. after addn. of benzoyl peroxide (1–5 g. per 1 g. of sample). After cooling, petr. ether is added, the mixt. is allowed to settle and the clear liquid is decanted. In connection with the development of this method, the influence of benzoyl peroxide on C_6H_6 solns. of rubber was studied more closely, and to this end pale crepe extd. with acetone and pptd. several times from C_6H_6 was used. With the Ostwald viscometer, the addn. of 1% benzoyl peroxide to 1% rubber solns. reduced the viscosity considerably, while the time required for this diminution depended upon the phys. conditions. Upon heating at 80° in daylight there was a 95% reduction in viscosity after 1 hr., while the viscosity of a corresponding soln. without benzoyl peroxide decreased only 26%. In diffused daylight the diminutions were 58 and 2%, resp. Similar results were obtained with solns. in darkness. Direct sunlight reduced the viscosity to such an extent that 1 day of exposure was about the same as 8 hrs. of heating at 80°. When the solns. with and without benzoyl peroxide were exposed to ultra-violet light in the absence of O, the diminutions in viscosity were of the same order of magnitude as those brought about by heating for the same length of time. The influence of benzoyl peroxide on rubber solns. is, therefore, greatly accelerated by ultra-violet light. The reduction in viscosity by benzoyl peroxide probably depends upon an attack on the double bonds of the rubber by O set free from the peroxide. Whether vulcanization with benzoyl peroxide is physically and chemically comparable with vulcanization with S remains uncertain. Expts. on this subject are in progress and will be published later. C. C. Davis

The standardization of the ozone test for rubber. E. P. Kearsley. *Rev. gén. caoutchouc* **7**, No. 62, 11–6(1930); *Gummi-Ztg.* **44**, 2078–9(1930).—The paper first discusses past work on the deterioration of rubber by light and air, where the chief destructive agent is O. This type of aging, which is manifest in the formation of a surface film and also by internal changes, becomes striking when the rubber is exposed under tension to O_3. A new method is described which makes it possible to subject rubber to a carefully controlled vol. and concn. of O_3 which can be reproduced in a reliable manner. A base mixt. of rubber 100, S 3, mercaptobenzothiazole 0.5, ZnO 5, was used to study the influence of various factors, such as the degree of elongation, time of elongation before treatment with O_3, the concn. of O_3, the time of treatment, degree of vulcanization, temp., moisture content and the addn. of various fillers in different proportions. The slight resistance to stress of the surface film formed by the action of O_3 on stretched rubber explains the appearance of a cracked surface. The resistance to stress is diminished so much that often 5–10% elongation is enough to produce cracking. The formation of cracks continues until the tension falls below this limiting value. The no. of cracks per unit surface depends upon the extent to which the tension exceeds that corresponding to the resistance to cracking, so that fewer cracks appear at low, than at high tensions. At high elongations the surface may become entirely covered with cracks. The size of the individual cracks depends upon the thickness of the surface film, and the latter increases with increasing concn. of O_3 temp. and time of treatment and also increases notably with addn. of gas black. Factors which influence the tensile strength of a rubber mixt. also influence the tendency to crack. The changes which occur during stretching previous to treatment with O_3 are attributed to changes in the state of stress of the mixt. during the elongation. When the equil. between the plastic and the elastic properties is reached these changes cease. With all mixts. which were studied, this equil. was reached at 100% elongation after 72 hrs. of stretching. The addn. of fillers has a pronounced influence on the formation of cracks, since the proportion and particle size of fillers have a great influence on the tensile properties of the mixt. If the elongation to which a rubber product is subjected in service is known, it should be possible to formulate the compn. of the rubber mixt. so that this elongation corresponds to the min. tendency to crack. The addn. of paraffin, which is used so extensively to minimize the tendency to crack, is only of limited effectiveness, since the surface film of paraffin (upon which the protection depends) is rubbed away in service. Data obtained during the investigation have shown beyond question that it is possible to obtain comparable results in the O_3 test by proper control of all factors which influence the action of the O_3. As a result it becomes possible to compare different types of vulcanizates in their resistance to cracking and to study the influence of various ingredients. Further research is necessary before this test can be correlated with natural aging. C. C. Davis

The compression of rubber. Some experimental results. F. Jacobs. *Caout-*

chouc & gutta-percha **27,** 15087–8(1930).—Quant. compression tests (using cubes) of vulcanizates of the solid-tire type and of the red-inner-tube type are described, with the results in graphical form. C. C. DAVIS

Autographic stress-strain curves of rubber at low elongations. A. A. SOMERVILLE, J. M. BALL AND L. A. EDLAND. *Ind. Eng. Chem., Anal. Ed.* **2,** 289–93(1930).—Following a discussion of present methods of obtaining stress-strain curves with dumb-bell and ring test pieces, a new method is described and illustrated which utilizes a new form of test piece. The latter has the form of a molded loop 10 in. long and of 0.25 × 0.25 in. cross section, and has at least 4 features which make it preferable to the present method: (1) The cross section is about 6 times that of ordinary test pieces and so more accurate readings particularly at low elongations are obtained. (2) Each individual loop is cured in molded form, so no cutting is necessary. (3) Flaws in a test piece are of no consequence. (4) Every part of the test piece is stretching at a const. speed throughout the test. The utility of the test is shown by stress-strain curves of rubber mixts. of the "pure gum" type and mixts. contg. C black, and these curves also show the effects of different states of cure, rate of extension, grain from the milling operation, flaws in the test piece, humidity, temp., and proportion of C black on the stress-strain curves. Temp. has the most influence on the results; the rate of extension and grain have less influence; and humidity plays no significant part. The value of the method lies in the fact that the low elongations which are measured correspond more closely than do ordinary methods to the service conditions of many rubber goods. C. C. D.

Organic coloring agents in the rubber industry. F. JACOBS. *Caoutchouc & gutta-percha* **27,** 15122–4(1930); cf. *C. A.* **24,** 4659.—The properties of various com. colors are tabulated. C. C. DAVIS

The coloring of rubber. Organic colors. F. JACOBS. *Rev. gén. caoutchouc* **7,** No. 61, 31–6; No. 62, 37, 39, 41, 43, 45, 47, 49, 51; No. 63, 31–5(1930); cf. *C. A.* **24,** 3922.—The colors include violets, blacks, blues, greens, yellows, oranges, reds and browns; their chemistry and their com. importance, and various methods of coloring rubber mixts. and latex are discussed. C. C. DAVIS

Carbon black in rubber insulating compounds. W. B. WIEGAND AND C. R. BOGGS. *Ind. Eng. Chem.* **22,** 822–6(1930).—Contrary to common belief and statements in the literature, C black not only has no deleterious effect on the insulating properties of rubber compds., but actually improves them in many cases. Expts. were carried out on 3 compds. in which whiting was replaced by C black in various amts. With a 40% rubber compd., the use of 3¼% C by vol. had the following effects: resistivity increased 68%; breakdown voltage increased 40%; dielec. const. increased 10% (d. c.); dielec. const. at 1000 cycles increased 14%; dielec. const. at 440,000 cycles increased 9%; power factor at 1000 cycles decreased 24%; power factor at 440,000 cycles decreased 19%. With a 30% compd. and with a 35% compd. contg. 22% reclaimed rubber, similar improvements were observed, but of less magnitude. These results indicate that specifications for insulating compds. should be revised to allow the use of C black. The optimum amt. must be detd. in each case, but is probably not more than 10%. This effect of C black is attributed to its ability to adsorb H_2O and dissolved electrolytes. I. H. ODELL

The dispersion of gas black and the physical properties of rubber mixtures. E. A. GRENQUIST. *Rev. gén. caoutchouc* **7,** No. 63, 17–22(1930); *Gummi-Ztg.* **44,** 2077–8 (1930).—Various investigators have called attention to the importance of the state of dispersion of fillers in rubber in obtaining the best phys. properties of the resulting mixts. In the present paper, the attempt is made to find a relation between the dispersion of gas black and the phys. properties of the mixt. The dispersion of gas black was followed microscopically with freshly cut surfaces of the unvulcanized and vulcanized mixts. The technic of this work is described in detail. The mixts. contained rubber, S, ZnO, gas black, accelerator, antioxidant, stearic acid and pine tar. A bad dispersion of gas black was obtained if gas black, ZnO and S were mixed into the still unsoftened rubber. By prolonged milling this bad dispersion could be improved, so that the fresh surface had a velvet appearance. However, after a certain time of mastication the dispersion became imperfect again, probably because of flocculation. Samples with a dull surface showed bad dispersion, whereas a highly lustrous surface indicated good dispersion. Plasticity measurements with the Williams plastometer were also made, and these showed that as the time of mastication was increased, the plasticity diminished at first (probably because of the stiffening effect of the gas black) and then increased in proportion to the time of mastication. The influence of mastication on the rate of vulcanization was then studied, and it was found that the max. tensile strength was always reached at the same cure, regardless of the extent of mastication. Prolonged mastication and the better dispersion resulting increased the

tensile strength and the modulus up to a certain time, beyond which these diminished with increasing times. The elongation diminished with increase in the time of mastication. Resistance to abrasion and the hardness increased up to a certain point of the mastication, and beyond this they diminished. The tensile strengths of samples aged in the Geer oven increased with the time of mastication and then diminished progressively. The problem then arose whether the improvements in the phys. properties depended upon improved dispersion or upon an increase in the strength of the rubber film. Detns. of the combined S showed, however, that with increasing degree of mastication the strength of the rubber phase diminished. The combined S increased steadily, while the phys. properties showed a pronounced max. after a definite time of mastication. It can therefore be concluded that the improved phys. properties are to a great extent a result of the improved dispersion resulting from prolonged mastication. The expts. show likewise that with any mixt. of rubber and gas black there is an optimum degree of dispersion at which the best phys. properties of the vulcanizates are obtained. C. C. DAVIS

The uses of resins in rubber manufacture. H. P. STEVENS AND W. H. STEVENS. *Brit. Plastics* **2**, No. 14, 68, 70, 72–3(1930).—A review and discussion with 16 references. C. C. DAVIS

Effect of keeping coagulum in serum on the plasticity of smoked sheet. ANON. Imperial Institute. *Trop. Agr.* (Ceylon) **73**, 7–9(1929).—In 1 series of expts. AcOH was used as coagulant and in another AcOH + *p*-nitrophenol. The coagulum remained in the serum for variable lengths of time from 4.5 to 55.5 hrs. in each series. At the end of 6 months' storage of the smoked sheet at 15°, mastication tests gave very uniform results with the samples from the *p*-nitrophenol set. The other set gave variable results, indicating but not proving that smoked sheet becomes less plastic when allowed to remain too long in the serum. Hardness tests after 6 months' storage at 5° and 15° with ordinary humidity showed little change, while samples stored in desiccators over H_2O or $CaCl_2$ hardened considerably, those prepared from coagulum kept for the shortest period in the serum hardening least. Moisture conditions during storage of unmasticated rubber are important. A rubber-S (90:10) mixt. vulcanized at 148° showed a progressive decrease in the time of vulcanization with the length of time the coagulum remained in the serum. In both series it decreased from 120 to 111 min. *p*-Nitrophenol had no effect on the tensile strength, and the latter was satisfactory in every case. A. L. MEHRING

Some properties of sponge rubber. ANON. *Bur. Standards Circ.* No. 377, 8 pp. (1929).—Thirteen samples of different types of sponge rubber from 5 manufacturers were tested for hardness, porosity, tensile strength, elongation, permanent "set," buoyancy in water, hysteresis under slow compression and under impact, thermal cond. and wt. per unit vol. to obtain information of general value on the properties of com. sponge rubber. Photographic enlargements of cross-sections of all samples are shown, the technic developed for the individual tests is described in detail and the results of the tests are given in tabular and graphical form. These results show that at least 3 types are manufactured, in 2 of which the cells are closed and in the other of which the cells are to a large extent open. The closed-cell types may be used for some purposes where the ordinary open-cell type is unsuitable. The phys. properties of sponge rubber depend both upon the texture and upon the compn. of the vulcanizate. The tensile strength and in most cases the elongation are low compared with ordinary soft vulcanizates. Softness is not a criterion of damping properties. Com. sponge may be obtained in various weights from 5 lb. per cu. ft. upwards. C. C. DAVIS

Method of making micro sections of rubber stocks. RAYMOND P. ALLEN. *Ind. Eng. Chem., Anal. Ed.* **2**, 311–3(1930).—The method was developed to fulfil the need of a rapid and convenient method of prepg. thin sections of rubber stocks. A barely visible piece of the rubber is cut with dissecting scissors and is squeezed between a microscope slide and cover glass in a pool of fused beeswax or rosin. If held in this position until hard the sectional slice remains thin. Sections only 1μ or even less can be made of stiff mixts. contg. 25–30% gas black, and of either vulcanized or unvulcanized mixts. Some applications are mentioned; illustrations show how to prep. the sections; and 6 typical rubber pigments are shown dispersed in rubber from which sections have been prepd. C. C. DAVIS

The protection of rubber articles after manufacture. The diffusion process. CHARLES MOUREU, CHARLES DUFRAISSE AND PIERRE LOTTE. *Rev. gén. caoutchouc* **7**, No. 63, 9–15(1930).—See *C. A.* **24**, 3396. C. C. DAVIS

Hard-rubber dust. Some of its applications and a comparison between hard rubber and synthetic powders in mixing. FRANK BATH. *Rev. gén. caoutchouc* **7**, No. 61, 37–43; No. 63, 23–9(1930); cf. *C. A.* **24**, 3129.—A review and discussion. C. C. D.

The influence of zinc oxide on the action of the principal accelerators of vulcanization. The preparation of transparent rubber. R. THIOLLET AND G. MARTIN. *Caoutchouc & gutta-percha* **27**, 15084–7(1930).—The base mixt., pale crepe 100, stearic acid 0.5, palm oil 1, was cured with 5, 1 and 0 parts of ZnO, resp., and in turn with 16 accelerators and the proper % of S, resp., and the vulcanizing properties, tensile properties, aging, transparency and tendency to bloom were detd. on the vulcanizates. The cures were at the characteristic temps. for times a little less than the times corresponding to the max. phys. properties from the point of view already described (cf. *C. A.* **24**, 1248, 3397). The mixts. contg. 5% ZnO cured in a normal manner and were opaque after vulcanization. In most cases the vulcanizates contg. 1% ZnO were transparent, but were not so when cured with Zn salts of org. acids. Where relatively high proportions of S were required with certain accelerators, the transparency was masked by the subsequent bloom. The phys. properties were nearly as good with 1% as with 5% ZnO, and the aging was the same. In some cases cures were obtained with no ZnO, but the phys. properties of the vulcanizates were much inferior to those contg. ZnO, particularly the aging properties (judged by aging in air at 70°). Certain accelerators, *e. g.*, Zn methylphenyldithiocarbamate and mercaptobenzothiazole, have little activity without ZnO, but become active in its absence upon addn. of 1 part of anhydroformaldehyde-aniline. The vulcanizates aged badly, however. The best aging was obtained with ethylideneaniline and *p*-nitrosodimethylaniline, but in spite of satisfactory transparency without ZnO, the vulcanizates were strongly colored and the phys. properties were poor. The differences in phys. properties with and without ZnO were greater with these 2 accelerators than with others. The results show that in general it is necessary to use ZnO as an adjuvant in curing with org. accelerators but that when transparent products are desired, it is practicable to use only 1% on the rubber with an accelerator which does not color the vulcanizate nor require so much S that blooming occurs. The following 4 mixts. are well adapted for transparent products: (1) pale crepe 100, S 1.8, tetramethylthiuram disulfide 0.4; (2) pale crepe 100, S 1.8, tetramethylthiuram monosulfide 0.4; (3) pale crepe 100, S 2.5, mercaptobenzothiazole 0.7; (4) pale crepe 100, S 2.5, mercaptobenzothiazole 0.3, diphenylguanidine 0.4; all 3 mixts. with ZnO 1, palm oil 1 and stearic acid 0.5. The cures are 8, 8, 35 and 30 min., resp., at 2, 2, 3 and 1.5 kg. steam pressure, resp.

C. C. DAVIS

Overflow during vulcanization, its dependence upon inactive and active fillers and errors in previous calculations of the specific gravity of vulcanizates resulting from it. RUDOLF DITMAR AND CARL H. PREUSSE. *Chem.-Ztg.* **54**, 501–2(1930).—A study of the changes in vol. which occur during the vulcanization was made with the base mixt.: smoked sheet 100, S 3, mercaptobenzothiazole 1, ZnO 5, filler (whiting, talc, gas black, animal charcoal, silica-gel) variable. On exposure to vulcanizing conditions, raw rubber did not increase in vol.; but with the mixts. above, there was an increase in vol. in every case, and the following general conclusions are drawn: (1) Whenever rubber is vulcanized with S there is an increase in vol. (2) Every inert filler influences this increase in vol. in a characteristic way. (3) An increase in the proportion of an inert filler influences the trend of the vol. increase curve in a manner characteristic of the filler. (4) Different inert fillers influence the vol. increase in different ways. (5) Active fillers (gas black) influence the vol. increase curve in a different way from inert fillers. (6) An increase in the proportion of an active filler influences the vol.-increase curve in a manner characteristic of the filler. (7) Different active fillers influence the increase in vol. in quite different ways. (8) The d. of a rubber mixt. vulcanized with S is always less than the d. of the unvulcanized mixt. (9) All calcns. of d. heretofore made in the rubber industry and any related theories are incorrect because they are based on the false assumption that no increase in vol. occurs during vulcanization. (10) Detns. of d. must be based on overflow detns.

C. C. DAVIS

Effect of curing temperature upon the properties of a rubber-sulfur mix. C. R. PARK. *Ind. Eng. Chem.* **22**, 1004–7(1930).—Data are presented covering a range of equiv. cures at 6 different temps. (135.5–62°) on a stock consisting of rubber 100, S 6.25. Within the temp. range the temp. of cure has no effect upon the quality of the vulcanized stock from this mix. Comparison is made of natural aging with artificial aging, and certain unexplained differences are found to exist in the results thus obtained. The temp. coeff. of vulcanization is detd. by 3 methods and found to be 2.50 per 10°. Various curves are given.

C. J. PEDERSEN

Rubber mills and Banbury mixers. CARL F. SCHNUCK. *Ind. Eng. Chem.* **22**, 1007–10(1930).—A general discussion of the designs and the materials of construction, and the conditions and the methods of operation of roll mills and Banbury mixers. The principles of the 2 types of machines are compared and it is pointed out that the Ban-

bury mixer is essentially a mixer and a compounder by which direct economies in labor and power are generally secured. Typical power curves of the 2 machines are given. C. J. PEDERSEN

Surface application of age resisters to cured rubber vs. mill incorporation prior to cure. W. L. SEMON, A. W. SLOAN AND DAVID CRAIG. *Ind. Eng. Chem.* **22**, 1001–4 (1930).—The results obtained show that the order of activity of the age resisters is essentially the same whether they are applied to the surface or milled into the rubber, but that for most purposes mill incorporation is preferable to surface application, although the latter method will retard deterioration even after it has once commenced. The various advantages obtained by the 2 methods are listed, and tables of data are given. C. J. PEDERSEN

Zinc oxide as a rubber pigment. ANON. *New Jersey Zinc Co., Research Bull.* 32 pp. May, 1930.—An illustrated Bull. dealing with the use and the general properties of ZnO in rubber compds. The following points are discussed: wettability, heat cond., heat capacity, activation, heat generation, rate of cure, reënforcement, aging, working qualities and color. The company products and processes are listed. A comprehensive bibliography of tech. papers and U. S., British and German patents is included. C. L. PEDERSEN

The long spacings of rubber and cellulose. G. L. CLARK AND K. E. CORRIGAN. *Radiology* **15**, 117–22(1930).—A new method is proposed for the examn. of highly polymerized compds. This consists in the direct measurement from diffraction interferences of colloidal micelle dimensions. The construction of an instrument consisting of an x-ray tube with Mg target and vacuum camera without intervening window or air space is described. The large value of the K α-line for Mg, 9.86 A. U., makes possible the registration of diffraction maxima usually fused with the primary beam spot on photographs made with Cu or other radiation. The major spacing of unstretched vulcanized rubber is 99.3 A. U. The no. of isoprene mols. per micelle is estd. to be of the order of 8000. Three measurements of the long spacings of cellulose are recorded as 274.1, 168.0, first and second orders, and 156.0. G. L. CLARK

The extraction of gutta-percha leaf. A. W. K. DE JONG. *Rec. trav. chim.* **49**, 827–40(1930).—The gutta-percha hydrocarbon can be obtained from the leaf by extn. with benzene at 25° and pptn. of the ext. with alc. or by extn. with light petroleum ether at about 35° and crystn. of the ext. at about 16°. According to the opinions of several factories the product obtained by cold extn. with benzene was of poor quality, contg. a great deal of low-grade gutta-percha. The product from the warm extn. was of better quality but still contained a fair proportion of low-grade gutta-percha. Probably the amt. of second-grade gutta-percha corresponds to the amt. sol. in benzene at ordinary temp., and the present investigation makes it probable that this so-called second-grade or immature gutta-percha consists of the same hydrocarbon as the first grade, but modified by melting and possessing smaller particles than the first grade. It was found that gutta-percha can exist in 3 forms possessing different solubilities. Immediately after melting a large proportion is sol. in light petroleum ether at ordinary temp.; after 1 or 2 days this soln. gives a ppt. which is easily sol. in benzene at room temp. (below 19°). On evapg. this soln. at room temp., a film is obtained which is only slightly sol. in benzene at room temp. The difference among these 3 forms of gutta-percha is attributed to different sizes of the particles; the difference in compn. cannot be great, the several specimens all melting at about the same temp. (61–4°; 62–5°). Shavings of gutta-percha melted in water at 62° may be drawn out to give threads, which shrink immediately in warm water, reproducing the shaving in its original length and breadth. Gutta-percha thus also possesses elasticity, not at ordinary temp., but in the neighborhood of its m. p., and the expt. with the shavings, mentioned above, led up to the idea that combinations of laterally oriented mols. slide along each other, mols. in a free state forming the lubricant. On cooling and crystn. the thread cannot shrink, but as the lubricant is formed once more by partial melting, the combinations of laterally oriented mols. move back. The manipulations can be repeated many times with the same shaving. For a detailed description of the numerous expts. on the solubilities of the 3 forms of gutta-percha as well as for the description of semi-technical extn. expts., including the recuperation of the solvents, reference is made to the original paper. C. F. VAN DUIN

The influence of rubber "resins" in zinc oxide-accelerator mixings. W. S. DAVEY. *J. Soc. Chem. Ind.* **49**, 338–42T, 343T(1930).—Expts. were made with acetone-extd. and unextd. rubber with 10 accelerators representing the various classes, and the results obtained confirm those previously obtained by Martin and Davey (*C. A.* **17**, 2203; **19**, 3037). It is still suggested that the function of the fatty acids is to prevent the flocculation of the ZnO and so increase the surface available for re-

action with the accelerator. This is important in mixings contg. low proportions of ZnO, but not in those contg. high proportions where there is much more than enough ZnO to satisfy the requirements of the accelerator. This is opposed to the views of Whitby and Evans (*C. A.* **22**, 3064) who consider that fatty acids are generally essential to vulcanization in the presence of large quantities of ZnO and that the function of the former is to form rubber-sol. Zn compds. which are capable of reacting with the accelerator. With mercaptobenzothiazole, acids are effective with all proportions of ZnO, and it is thought that its behavior in the presence of large amts. is due to its relatively slow soly. and tendency to form flocculates, which limits its sphere of action and consequently its interaction with insol. ZnO. The amt. of fatty acid naturally occurring in rubber is of the most importance in mixings contg. about 5 parts of ZnO. It does not seem likely that first-grade plantation rubber will cause serious variation because of the amt. of acid in the rubber. Curves and tables of data are given. C. J. P.

A preliminary investigation of the effect of different conditions of storage on the hardness of raw rubber. G. MARTIN. *Trop. Agr.* (Ceylon) **74**, 342–6(1930).—Samples of rubber were stored for 11 months under varying conditions of temp., relative humidity and gases composing the atm. In very dry or very damp atms. the rubber hardened considerably. At a relative humidity of about 80% the rubber remained at nearly the same degree of hardness. When stored in O it hardened more than when kept in N. A. L. MEHRING

Temperature measurements in the rubber industry. CONTI GIAMPIETRO. *Industria chimica* **5**, 296–303(1930).—A summary of the various processes used in the rubber industry: washing of rubber, mixing, calendering, vulcanizing, etc., emphasizing the various temp. measuring, recording and control devices needed in the various operations, with a description of each. A. W. CONTIERI

Report on the market possibilities of fractionally coagulated crepe. G. MARTIN. *Trop. Agr.* **74**, 336–41(1930).—Three samples of crepe rubber were prepd. No. 1 was made in the usual way as a control, No. 2 by pptg. only about 10% of the rubber from latex and No. 3 by coagulating the remaining 90%. No. 2 became vulcanized in a little over half the time and maintained good tensile strength over a much wider range of cures than did Nos. 1 and 3. No. 2 gave better results in aging tests, but all 3 samples behaved similarly in plasticity tests. These results are surprising, since No. 2 was dark colored, was given a low value by professional appraisers, contained a larger percentage of material not rubber and showed poor coherence when freshly prepd. No. 3 was very light in color and should be superior for the manuf. of transparent rubber goods. A. L. MEHRING

Methods of evaluating so-called "English sheet" or sawed sheet rubber. PAUL BOURGEOIS. *Chimie & industrie* **Special No.**, 401–11(March, 1930).—The manuf. and tests of this type of rubber are described. A. PAPINEAU-COUTURE

Coloring of rubber. F. JACOBS. *Rev. ind.*, **60**, 427–39, 492–504(1930).—A general discussion of the problem with a review of the chem. principles necessary for a clear understanding of the process and notes on mineral and org. colorants and their use. E. I. S.

The kinetics of the vulcanization of rubber. BIRGER W. NORDLANDER. *J. Phys. Chem.* **34**, 1873–1902(1930).—The rate of vulcanization of rubber when no accelerator is used is defined by the rate of formation of combined sulfur, $dS_c/dt = k_3[S_\mu][R]$, where S_c = combined S, $[S_\mu]$ = concn. of active S_μ R = concn. of rubber in g./100 g. of mix, and RS_c = vulcanized rubber. The rate of vulcanization due to accelerator action is $dV_4/dt = k_4[A][S_\mu].100$, where $[A]$ = concn. of accelerator A in g./100 g. of mix. The reaction rate at various temps. varies as $[S_\mu]$. The heat of activation, E, of the rubber-sulfur reaction, calcd. from the Arrhenius equation, $\log k = C - E/4.57T$, is 27,000 cal., and E for the accelerator sulfur reaction is 25,000 cal. This suggests that the same process, activation of S, is involved in both cases. By using the calcd. value of E in the Boltzmann distribution equation, $f = e^{-E/RT}$, the fraction, f, of mols. in the activated state at temp. T is found to be 10^{-14}. Conclusion: *Activated* S_μ *mols.* take part in the reaction. The mechanism of the vulcanization process is considered to involve adsorption of sulfur on rubber and chem. combination of activated S_μ with rubber. The vulcanizing agent in cold vulcanization is activated amorphous S_μ. S. LENHER

Precautions to be taken in the storing of raw materials. ALBERT HUTIN. *Rev. gén. mat. plastiques* **6**, 485(1930).—The chief precautions which should be taken in the storing of raw, regenerated and waste *rubber* are outlined. A. PAPINEAU-COUTURE

The development of rubber reclaiming since the War and its importance in the rubber industry. PAUL ALEXANDER. *Gummi-Ztg.* **44**, 2396–8(1930); cf. *C. A.* **23**, 306.—A review and discussion, for the most part economic. C. C. DAVIS

Mixing mills, mixing machines and mixing. PETER WERNER. *Gummi-Ztg.* **44**, 2446–9, 2492–4(1930).—A review and discussion. C. C. DAVIS

Hard rubber and some of its unusual applications. D. E. JONES. *Rubber Age* (N. Y.) **27**, 537–8(1930).—Descriptive. C. C. DAVIS

Wild rubber of the Amazon. JOHN C. TREADWELL. *India Rubber World* **82**, No. 6, 57–60(1930).—An illustrated review and a discussion of rubber from the Amazon in comparison with plantation rubber, both on a basis of quality and of economics. C. C. DAVIS

Spanish rubbers. MARIANO TOMEO AND J. GARCIA-VIANA. *Inst. forestal de investigaciones y experiencias* **3**, No. 6, 163–70(1930).—Two samples of latex from the Canary Islands and one from Spanish Guinea were analyzed for H_2O, ash, resins, albumins, $PhNO_2$ soly. and acidity. The results showed the contents of rubber in the crude latex to be 27.1, 14.2 and 12.0%, resp., and the resin contents to be 56.5, 75.0 and 58.0%, resp. Densities of the samples after washing with H_2O at 70° for 2 hrs. were 1.056, 1.040 and 0.991, resp. Losses during washing were 29, 5 and 40%, resp. The high percentages of resin permitted ready soln. in C_6H_6. The resins proved to be of the Angola gum and mastic types. The latex contained no essential oils. A photomicrograph of the Guinea latex is reproduced. Vulcanization of this latex does not yield a satisfactory product, and it can be used commercially only in quantities of 5–10% together with latex contg. less resin. Species of *Euphorbia* which produce this latex are briefly discussed. H. K. SALZBERG

Developments in sprayed rubbers. ERNEST HOPKINSON. *Bull. Rubber Growers' Assoc.* **12**, 495–8(1930).—Descriptive, including quant. data on the mastication, resistance to tear and aging of sprayed rubbers. C. C. DAVIS

Rubber and the mechanical testing of soft rubber. RICH. AMMON. *Chem.-Tech. Rundschau* **45**, 761, 782, 803(1930).—A discussion of methods of manuf. and app. and methods for detn. of ductility, elasticity, hardness, etc. E. PICKERING

Flexing machine for rubber testing. E. W. BOOTH. *India Rubber World* **82**, No. 6, 53–5(1930).—A new app. is described and illustrated, in which tire tread mixts. may be flexed under a const. load per unit area and at a definite temp. With this machine the effect of various ingredients, such as antioxidants and accelerators, can be studied, and though the results cannot be compared quantitatively with service tests, the relative influence of individual substances of a particular class can be studied. C. C. DAVIS

Early stages of oxidation in rubber—a quantitative application of the pyrrole test. J. W. TEMPLE, SIDNEY M. CADWELL AND MORRIS W. MEAD, JR. *Ind. Eng. Chem., Anal. Ed.* **2**, 377–80(1930).—The pine splint-HCl test for the oxidation products of rubber has been developed in a quant. way. The technic and the app. are described. Data from the application of the test to a wide range of com. stocks are given. Its use in following the early stages of oxidation as they occur in accelerated aging of vulcanized rubber is described, and attention is called to an apparent difference between O_2 and heat aging. Evidence is cited that the substance which gives the test, probably levulinic aldehyde, is formed independently of, and previous to, the actual phys. deterioration of the rubber. C. J. PEDERSEN

Cleaning rubber by straining. J. P. MAIDER. *India Rubber World* **82**, No. 6, 56 (1930). C. C. DAVIS

The vulcanization of rubber and the theories of vulcanization. A. BARAZETTI. *Rev. gén. mat. plastiques* **6**, 283–90, 323–33(1930).—A review. A. PAPINEAU-COUTURE

Latest applications of the Vulcalock process in industry. H. E. FRITZ. *Rubber Age* (N. Y.) **27**, 587–8(1930).—An illustrated description. C. C. DAVIS

The manufacture of molded rubber articles. I. Raw materials. II. Mining and vulcanization. T. L. GARNER. *Brit. Plastics* **2**, 53–4, 101–2, 158, 160(1930). E. J. C.

Notes on the manufacture of rubber-insulated cables. ERNST ADEL. *Gummi-Ztg.* **44**, 2310–12(1930); cf. *C. A.* **23**, 2513.—A discussion of some mech. and chem. mfg. problems. C. C. DAVIS

Patents

Rubber. THE ANODE RUBBER CO. Ger. 500,643, July 19, 1925. See Brit. 257,885 (*C. A.* **21**, 3141).

Treating rubber latex. EARDLEY HAZEL (to Dominion Rubber Co., Ltd.). Can. 302,996, Aug. 12, 1930. An alkali hypochlorite is added to latex with stirring and subsequently $Na_2S_2O_3$ is added. This improves the tackiness of the rubber.

Extrusion apparatus for making rubber tubes, etc., from concentrated latex. DUNLOP RUBBER CO., LTD., C. HAYES and E. A. MURPHY. Brit. 326,496, Nov. 14, 1928. Structural features.

Reducing the aging of rubber. I. G. FARBENIND. A.-G. (Walter Kropp and Leo Rosenthal, inventors). Ger. 501,642, Sept. 11, 1928. The life of vulcanized or unvulcanized, natural or synthetic rubber is prolonged by adding indanephenol, its substitution products or salts. The rubber so treated resists the action of the sun and air. The indanephenol may be prepd. after the method of 499,825 (*C. A.* **24**, 4524). Thus, a mixt. of smoked sheets, soot, ZnO, diphenylguanidine, S and resorcylindane is heated for 40 min. at $3^1/_2$ atm. The fresh rubber so formed has a solidity per kg./sq. cm. of 199 and an elasticity of 594%. If artificially aged 5 yrs., the corresponding values are 207 and 530. The same rubber without the resorcylindane addn. has a solidity of 240 kg./sq. cm. and an elasticity of 560% when fresh, but the figures after 5 yrs.' aging are 145 and 365, respectively.

Hardening gutta percha and similar materials. W. S. SMITH, H. J. GARNETT and J. N. DEAN. Brit. 326,481, Dec. 12, 1928. The material is subjected to a regulated heating at temps. which may rise to about 50–55°, and is thus rendered denser, less affected by water and vapors such as those of tar, and less liable to "sweat" and its elec. constants are rendered more stable.

Rubber products from aqueous dispersions or emulsions. DUNLOP RUBBER CO., LTD., W. H. CHAPMAN and D. W. POUNDER. Brit. 326,497, Nov. 14, 1928. Aq. emulsions or dispersions which are gelled rapidly by heat are made into tubes, strips, sheets or other forms and gelled by treatment with a suitable fluid heating medium such as steam or hot water. If necessary the material used may be rendered more sensitive to the treatment by addn. of substances such as NH_4 persulfate, with or without trioxymethylene, and Na_2SiF_6. Several examples are given. Cf. *C. A.* **23**, 4596.

Rubberized fabrics. DEUTSCHE GASGLÜHLICHT-AUER-G. M. B. H. Ger. 501,718, Nov. 1, 1927. Pliable colored, rubberized materials are obtained by mixing TiO_2 with the dye and embodying the mixt. in the rubber prepn. The process is particularly applicable to light colors. For a lilac-colored effect, a mixt. of 1-*p*-toluinoanthraquinone and TiO_2 are embodied in a mixt. of crepe rubber, white factis, chalk and ZnO. The mixt. is emulsified in C_6H_6 and vulcanized by a S_2Cl_2-CS_2 soln. A green effect is obtained by a mixt. of crepe rubber, white factis, TiO_2, S, Zn ethylphenyldithiocarbamate, phenyl-β-naphthylamine and di-1-naphthyl sulfide, emulsified in C_6H_6 and vulcanized by exposure to air.

Rubber sheeting, etc. DUNLOP RUBBER CO., LTD., W. H. CHAPMAN and D. W. POUNDER. Brit. 326,782, Nov. 14, 1928. In forming products such as rubber sheeting or rubber-coated fabrics, heat-sensitive aq. rubber dispersions are subjected to calendering between 2 face sheets and the dispersions are afterward caused to gel by leading the facing sheets into a heating fluid medium such as hot water, oil, steam or hot air. The face sheets may, if desired, be treated to prevent adhesion of the rubber sheeting or may be caused to unite by the rubber to form "double texture waterproofed fabrics." Various details and modifications of the procedure are described.

Lining tanks with rubber. ALLAN B. MERRILL (to B. F. Goodrich Co.). U. S. 1,772,190, Aug. 5. Various details of procedure are described suitable for lining industrial tanks such as those for storage of corrosive chemicals after the tanks are in operative position in a factory.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 326,869, Dec. 20, 1928. Polymerization of butadiene or its homologs, phenylbutadiene, styrene, etc., by an alkali metal such as Na is effected in the presence of a small quantity of NH_3 or of a free cyclic or satd. aliphatic primary, secondary or tertiary base which slows down the polymerization and avoids undue rise of temp. Various details and examples of procedure are given.

Aldehyde-amine condensation products. CLAYTON ANILINE CO., LTD., and H. FRITZSCHE. Brit. 326,525, Nov. 12, 1928. Condensation products such as may be used as *rubber vulcanization accelerators* are produced by the reaction of more than 1 mol. proportion of an aldehyde such as CH_2O, acetaldehyde or crotonaldehyde with the condensation product of a primary or secondary amine and an aldehyde-bisulfite compd. such as Na aniline methane-ω-sulfonate or Na aniline ethane-ω-sulfonate or by causing the aldehyde to react with a mixt. of the amine and the bisulfite. Several examples are given, including an example of a rubber compn. in which the product is used.

Vulcanization accelerator. SIDNEY M. CALDWELL and ALEXANDER T. MAXIMOFF (to Dominion Rubber Co., Ltd.). Can. 302,995, Aug. 12, 1930. Heptaldehyde and aniline are mixed at 135° to 145°, held at this temp. until max. strength has been reached, and then steam-distd. The product is a vulcanization accelerator.

Vulcanization of rubber. WINFIELD SCOTT (to The Rubber Service Laboratories Co.). Can. 303,468, Aug. 26, 1930. Rubber and S are heated in the presence of a vulcanization accelerator comprising the reaction product of an alkylidenearylamine and α-ethyl-β-propylacrolein. Cf. *C. A.* **24**, 3926.

Vulcanization of rubber to leather. LEON B. CONANT. Ger. 500,642, July 12, 1927. See Brit. 275,194 (*C. A.* **22**, 2292).

Thickening and stabilizing latex. MERWYN C. TEAGUE (to American Rubber Co.). U. S. 1,772,647, Aug. 12. A compounded latex contg. not less than about 60% solids is treated with saponin in excess of 0.5 part for each 100 parts of rubber.

Treating latex. JOHN MCGAVACK (to Naugatuck Chemical Co.). U. S. 1,772,752, Aug. 12. A method of creaming latex is described which comprises diluting latex to a solids concn. of about 30–32% and adding NH_4 alginate, allowing the latex to cream, using serum sepd. from the latex to dil. a fresh portion of latex to about 30–32% solids concn. and creaming the latter with NH_4 alginate, then removing the latex cream and repeating the NH_4 alginate creaming operation upon successive fresh portions of latex with serum as a diluent. U. S. 1,772,753 relates to preserving latex with a small quantity of a suitable salt of an acid contg. O and either Se or Te. Cf. *C. A.* **24**, 3924.

Aqueous emulsions of rubber, balata or gutta-percha. WM. B. PRATT (to Dispersions Process, Inc.). U. S. 1,775,569, Sept. 9. Rubber or like material and S are dissolved (suitably in C_6H_6) together with oleic acid, and water contg. sufficient NH_3 to saponify the oleic acid is then added until a change in phase occurs, and the rubber or like material and S are dispersed in the water; the solvent is then removed at a temp. which does not cause recoagulation of the dispersed rubber. Cf. *C. A.* **24**, 2916.

Coagulated products from aqueous rubber dispersions. DUNLOP RUBBER CO., LTD., E. A. MURPHY and D. F. TWISS. Brit. 327,451, Jan. 5, 1929. Aq. rubber dispersions and the like are coagulated to a crumb-like or powd. form by the addn. of fillers such as gas black, clay, silica and whiting in the presence of a protective colloid such as NH_4 oleate or resinate, or by the subsequent addn. of the same or other fillers such as ZnO, CaO or MgO in sufficient quantity to lower the anti-coagulant effect of the colloid. The crumb-like product may be dried, pressed and used directly to form *leather-like products* contg. a large proportion of a filler such as gas black, or may be used in other mfg. processes.

Coagulating rubber deposits. DUNLOP RUBBER CO., LTD., R. F. MCKAY and W. G. THORPE. Brit. 328,015, Jan. 16, 1929. A former is dipped in a rubber dispersion, and coagulation of the resulting deposit is effected by a spray or gaseous current of a coagulating medium. Successive coats may be applied, with intermediate layers of fabric or metal, etc.

Electrophoretic deposition of rubber from aqueous dispersions. C. MACINTOSH & CO., LTD., H. C. YOUNG and C. HEMM. Brit. 327,452, Jan. 5, 1929. In deposition on articles having closely grooved, corrugated or ribbed surfaces or deep reëntrant angles, uniform thickness is attained by depositing a thin preliminary coating, treating the deposit to give it a high specific resistance throughout, as by partial drying or washing, and then effecting further deposition. Alternatively, a dispersion with a high NH_3 content may be used for the preliminary deposition initially to form a deposit of high resistance.

Rubber compositions. IMPERIAL CHEMICAL INDUSTRIES, LTD., S. COFFEY and W. J. S. NAUNTON. Brit. 328,115, Apri 18, 1929. As "anti-agers" there are used org. compds. capable of dissocn. into free radicals contg. bivalent N such as tetraphenylhydrazine and *N*-triphenylmethyldiphenylamine.

Coloring rubber articles. ARTHUR P. WITTEN (one-half to George E. Hall). U. S. 1,774,781, Sept. 2. A rubber article is immersed through floating layers of transparent rubber soln. and of colored rubber soln. floating on a bath, so that the color layer is caused to adhere to the article and the transparent layer forms an overlying coating; the article is removed and vulcanized.

Variated surface effects on rubber articles. JAMES B. CROCKETT (to Cambridge Rubber Co.). U. S. 1,773,724, Aug. 26. A deposit of aq. rubber-contg. material such as a latex mixt. having a high percentage of incorporated mineral filler (such as ZnO and "chrome-tone yellow") is dried at temps. above 65° to produce checks or cracks in a variated fashion over the surface, and aq. rubber-contg. material of a different color is then applied and dried.

Apparatus for masticating rubber, etc. RICHARD C. LEWIS (to Farrel-Birmingham Co.). U. S. 1,773,367, Aug. 19. Structural features.

Apparatus for masticating rubber, etc. RICHARD C. LEWIS (to Farrel-Birmingham Co.). U. S. 1,773,428, Aug. 19. Structural features.

Bonding rubber to metal. HAROLD GRAY (to B. F. Goodrich Co.). U. S. 1,774,-

324, Aug. 26. A metal surface such as steel is coated with a film contg. a reaction product of a substance such as tung oil, linseed oil, castor oil or rosin oil with a strong inorg. non-oxidizing acid such as H_2SO_4 or HCl or a compd. such as a sulfate or chloride capable of undergoing thermal or hydrolytic dissocn. to form such acids; a rubber compn. is then applied to the coated metal, and the assemblage is subjected to heat and pressure. Cf. *C. A.* **24,** 265.

Attaching rubber to metals (as in lining tanks). DUNLOP RUBBER CO., LTD., H. C. YOUNG and C. HEMM. Brit. 327,856, April 10, 1929. The rubber is pressed onto the metal surface by mech. vibratory means. Various mech. and elec. details are described.

Cricket bat blades of rubber composition. J. HARRIS. Brit. 327,513, Feb. 18, 1929. Details of bat manuf. are described which may involve the making of the blades of a compn. comprising fresh or reclaimed rubber 1, granulated cork or wood shavings or sawdust 4 parts and vulcanizing ingredients such as S and PbO to give the desired hardness or resiliency.

Threads and foils of synthetic rubber. I. G. FARBENIND. A.-G. Brit. 327,164, Nov. 17, 1928. Threads, foils, etc., prepd. from solns. of synthetic polymerization products of diolefins with or without natural rubber, gutta-percha, balata, resins, cellulose derivs. and fillers are treated with a sulfurizing agent such as S chloride at a temp. not exceeding 100°, after their formation from initially purified solns. Various details of procedure are described.

Dentures of vulcanized rubber. AMBROSE STROE. U. S. 1,774,907, Sept. 2. Various details of manuf. are described.

Vulcanizing rubber. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,773,379, Aug. 19. "Age-resisting" properties of rubber are improved by incorporating with it, before vulcanization, a S reaction product of the condensation product of butylaldehyde and phenol. Cf. *C. A.* **24,** 4960.

Rubber vulcanization. BENJAMIN S. GARVEY (to B. F. Goodrich Co.). U. S. 1,774,322, Aug. 26. Vulcanization is effected of a compn. comprising rubber, a vulcanizing agent such as S, ZnO, a metallic thiocarbonate such as that of Ba and a substance such as piperidine-formaldehyde which reacts with CS_2 to form a rapid accelerator.

Use of rubber latex in binding paper leaves in book form. A. L. GRAMMER. Brit. 328,559, Jan. 25, 1929. The paper leaves are fanned or opened out at the binding edge, and rubber latex is applied by brushing or spraying. The latex may be treated with NH_3 or other substance to prevent premature coagulation.

Chlorinating rubber. M. DESENISS and A. NIELSEN. Brit. 328,818, May 16, 1929. Chlorination of rubber in soln. or dispersion is effected at a temp. of 80° or higher (suitably by introducing Cl into a soln. of rubber in CCl_4). In treating vulcanized rubber, the S may be eliminated as S chloride. The product may be made into films, filaments, etc.

Rubber compositions. I. G. FARBENIND. A.-G. Brit. 328,812, May 13, 1929. Lamp black is preliminarily incorporated with a liquid polymerizable polymerization product such as partially polymerized butadiene or partially polymerized vinyl chloride or acetate, and the mixt. is incorporated with rubber.

Forming flooring of rubber composition. JOHN B. LOSEY and WALTER R. STONE. U. S. 1,775,646, Sept. 16. App. is described.

Rubber articles. THE ANODE RUBBER CO. (ENGLAND) LTD. Fr. 684,422, Nov. 5, 1929. In making rubber articles from aq. dispersions of rubber, harmful materials imprisoned in the coagulated rubber and contained in the layer of rubber freshly coagulated, obtained by electrophoresis or by immersion, are eliminated before drying by solvents not attacking the rubber. Cf. *C. A.* **24,** 4665.

Rubber or like articles. THE ANODE RUBBER CO. (ENGLAND) LTD. Fr. 684,979, Nov. 14, 1929. See Brit. 326,497 (*C. A.* **24,** 4959).

Thin-walled rubber articles. DOROGI ÉS TÁRSA, LTD. Hung. 99,408, Apr. 11, 1927. The thinnest layer of thin-walled rubber articles is protected by a film of elastic, insol. varnish-like material.

Rubber products from dispersions. DUNLOP RUBBER CO., LTD., C. HAYES, E. W. MADGE and F. C. JENNINGS. Brit. 329,381, Feb. 19, 1929. Processes such as spreading, dipping or extrusion are effected with mobile aq. dispersions such as latex admixed with a small quantity of phenol or the like, with or without a tanning agent, and which may contain the usual vulcanizing agents and accelerators, etc., and subsequently treated with a reagent such as CH_2O to promote uniform gelling. Cf. *C. A.* **24,** 5181.

Depositing rubber, etc., from dispersions. DUNLOP RUBBER CO., LTD., R. F. MCKAY and E. W. MADGE. Brit. 328,980, Nov. 9, 1928. Rubber, gutta-percha or balata is deposited from a dispersion contg. no electrolytes, except those normally

present or used as preservatives or such as are normally used in the prepn. of artificial dispersions, by immersing 2 dissimilar electrodes in the dispersion (the anode may be a pure Zn plate and the cathode a Leclanché porous pot), connecting the electrodes together and allowing the assembly to stand until the required thickness of deposit is formed on the anode. The dispersions may contain addns. such as vulcanizing agents or dispersions of natural resins, synthetic resins or cellulose esters. Several examples are given. Cf. *C. A.* **24**, 2638.

Coating chemical apparatus with rubber. DUNLOP RUBBER CO., LTD., and D. F. TWISS. Brit. 328,686, Feb. 5, 1929. Parts such as pipes, vats, rollers, woven wire or perforated metal are sprayed with aq. rubber dispersions or aq. dispersions of like materials such as gutta-percha, balata or similar materials or rubber waste or reclaim, which may contain various specified vulcanizing and other ingredients. Cf. *C. A.* **24**, 5181.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 329,000, Jan. 5, 1929. Soft films prepd. from synthetic polymerization products of diolefins (which may be vulcanized and may contain rubber, softening agents, fillers, etc.), are treated with O or with O-contg. gases or agents (suitably with heat and pressure). Coatings such as those of vessels, stirrers or bobbins used in the manuf. of artificial silk are prepd. by applying a dispersion of the material in an org. solvent and treating with O.

Antioxidant or age resistor. ALBERT M. CLIFFORD (to The Goodyear Tire and Rubber Co.). Can. 303,838, Sept. 9, 1930. Certain amino derivs. of naphthoquinones are highly satisfactory as age resistors in treating rubber, *e. g.*, "2-hydroxy-1,4-anilinonaphthoquinone." Cf. *C. A.* **24**, 3674.

Triphenylmethyl dialkyldithiocarbamates. SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,775,985, Sept. 16. In making esters of this type (which are *rubber vulcanization accelerators*) such as triphenylmethyl ester of diethyldithiocarbamic acid, a soln. of a metallo salt (suitably the NH_4 salt) of the dialkyldithiocarbamic acid is treated with triphenyl chloromethane, the materials are heated until reaction is completed, followed by cooling and crystn. The triphenylmethyl diethyldithiocarbamate, m. 153°, is "fairly sol." in hot alc. and less sol. in cold alc. and $CHCl_3$.

Vulcanization accelerators. IMPERIAL CHEMICAL INDUSTRIES, LTD., S. COFFEY, W. J. S. NAUNTON and A. SHEPHERDSON. Brit. 329,456, April 4, 1929. Rubber and the like and vulcanizable oils are vulcanized in the presence of an N,N-dithio deriv. of a secondary amine such as N,N-dithiopiperidine (*Ber.* **28**, 165 *et seq.* (1895)).

Apparatus for vulcanizing rubber soles to uppers. BRITISH UNITED SHOE MACHINERY CO., LTD., and F. RICKS. Brit. 329,409, Feb. 27, 1929. Structural features.

Porous vulcanized rubber articles. M. WILDERMAN. Brit. 328,273, Dec. 20, 1928. Filters, diaphragms and the like are made by vulcanizing particles having a semi-vulcanized surface and which are maintained at such a temp. that they do not stick together during spreading into the molds. The particles are compressed and are vulcanized under such conditions that no moisture reaches them and at such a speed that strong bodies are formed. Brit. 328,274 relates to app. and procedure for making similar products.

Rubber. THE ANODE RUBBER CO., LTD. Ger. 503,646, May 6, 1927. The direct production of rubber goods from latex by immersion is described. Cf. *C. A.* **24**, 1249.

Conservation of rubber latex. I. G. FARBENIND. A.-G. (Curt Schuster and Heinrich Hopff, inventors). Ger. 503,645, Apr. 21, 1927. The latex is treated with water-sol. neutral or alk. salts of ester acids of mineral acids such as diarylphosphoric acid, Me_2SO_4, etc., by themselves or together with other conserving agents. In the example, latex is stirred with Na dicresyl phosphate. The latex then shows no tendency to coagulate. NH_4 diphenyl phosphate, $KMeSO_4$, etc., may be used. Other conserving agents such as NH_3, amines, alc., etc., may also be added.

Treating rubber latex. THE NAUGATUCK CHEM. CO. Ger. 505,172, Oct. 13, 1927. See Brit. 282,011 (*C. A.* **22**, 3805).

Treating rubber latex. JOHN MCGAVACK (to Naugatuck Chemical Co.). U. S. 1,777,045, Sept. 30. The rubber-contg. portion of latex is sepd. by allowing the latex to cream after treatment with an org. colloid and a small proportion of a latex coagulant, which is used in quantity too small to effect coagulation, followed by removal of the aq. portion and recovery of an uncoagulated rubber dispersion. Use of pectin and org. acids, etc., is described. Cf. *C. A.* **24**, 5181.

Preserving latex and rubber. I. G. FARBENIND. A.-G. Brit. 329,969, Feb. 27, 1929. Products especially suitable for storing are prepd. by adding preservatives or "anti-agers" in a dissolved or emulsified form, to latex or latex-like products before or during coagulation and in quantity approx. 0.5–2% that of the rubber; *e. g.*, there

may be added to an emulsion of synthetic rubber prepd. as described in Brit. 312,201 (*C. A.* **24**, 1249–50) an emulsion prepd. by dissolving the condensation product of acetaldehyde and toluidine in C_6H_6, stirring with triethanolamine contg. a small proportion of oleic acid and adding water.

Coagulating latex. Società italiana Pirelli and U. Pestalozza. Brit. 330,520, March 6, 1929. An aromatic disubstituted guanidine such as *sym*-diphenylguanidine, phenyl-*o*-tolylguanidine or di-*o*-tolylguanidine is used as coagulant in the process described in Brit. 284,608 (*C. A.* **22**, 4877) in which latex-contg. compns. contg. small quantities of coagulants are submitted to local heating to cause thickening and coagulation. About 0.5–2.5% of the substituted guanidine may be used and the temp. may be raised to 70–95°; vulcanizing ingredients, salts of NH_4 or of alk. earths or other bi- or tervalent metals may be added but are not required.

Forming and solidifying foam from rubber latex. Frederick H. Untiedt. U. S. 1,777,945, Oct. 7. Foam is formed from latex contg. a foam stabilizing agent such as soap and of such a character that a layer of the foam yields upon drying a porous rubber product; solidification of the rubber is effected, suitably by permitting the material to dry in sheets.

Rubber articles from latex or other aqueous dispersions. Dunlop Rubber Co., Ltd., C. Hayes, E. W. Madge and F. H. Lane. Brit. 330,536, March 8, 1929. In processes which may involve dipping, spraying, spreading, molding, extruding, etc., the rubber is caused to gel in a controlled time, which decreases with rise of temp., by adding CH_2O in excess of that required to neutralize the alky. of the dispersion, with or without addn. of a sensitizing agent such as $ZnSO_4$, $(NH_4)_2SO_4$, NH_4Cl or NH_4 oxalate, citrate or tartrate.

Rubber articles from dispersions. Dunlop Rubber Co., Ltd., G. W. Trobridge and E. A. Murphy. Brit. 330,970, March 21, 1929. In forming articles by spraying, dipping, spreading or pouring, when sharply-defined molding on the side next to the former is not required, the formers are coated with a liquid film of dehydrating and setting character such as is described in Brit. 303,544 (*C. A.* **23**, 4596) before the application of the dispersion. NH_4OAc, NaCl and NH_4Cl may be used and various details and modifications are described. Cf. *C. A.* **24**, 5535.

Maintaining uniformity of aqueous dispersions such as rubber latices. Paul Klein, Andrew Szegvari and Stephen Gotleb (to American Anode, Inc.). U. S. 1,777,646, Oct. 7. In treating materials which are liable to undergo coagulation by the influence of shock or agitation, there is imparted to substantially an entire body of the material, in a vat or receptacle, a general continuous upward movement by withdrawing the dispersion at or near the surface and reintroducing it at or near the bottom of the vat or receptacle. App. is described.

Rubber dispersions. Soc. K. D. P., Ltd. Fr. 685,746, Nov. 29, 1929. Rubber dispersions, to produce a product which may be dissolved again, are concd. in the presence of hydrotropes other than soaps and salicylates, *e. g.*, the K salt of 2,3-hydroxynaphthoic, 2,1-hydroxynaphthoic, sulforicinic, sulfanilic or *o*-hydroxyquinoline-carboxylic acid.

Apparatus for circulation of materials such as rubber dispersions in order to prevent segregation. Robert F. McKay, Harry Willshaw, Walter G. Gorham and Roger F. Lee (to American Anode, Inc.). U. S. 1,777,648, Oct. 7. Structural features.

Rubber articles from partially coagulated rubber films. B. W. Rowland (to Goodyear Tire & Rubber Co.). Brit. 329,897, Nov. 10, 1928. A film of rubber coagulated on the outer side only is applied to a form and the film is then treated with a coagulant to coagulate the other side. App. is described, and HOAc may be used as a coagulant.

Electrophoretic preparation of hollow rubber goods. The Anode Rubber Co., Ltd. Ger. 503,644, April 15, 1926. Caoutchouc is pptd. on anode molds by means of a depolarizing cathode.

Sponge rubber. Thomas W. Miller (to Faultless Rubber Co.). U. S. 1,778,270, Oct. 14. Mech. features.

Coloring rubber and similar materials. I. G. Farbenind. A.-G. Brit. 329,761, March 28, 1929. Rubber, gutta-percha, balata or the like is subjected to mech. working with a water-insol. coloring material in the form of an aq. suspension or paste contg. a small quantity of one or more org. substances more difficultly evapd. than water, such as AmOH, BuOH, benzyl alc., glycol, glycerol, cyclohexanol, glycerol acetates, triaryl phosphates, ethylene glycol, alkyl or aryl ethers, cyclohexanone, triethanol amines, xylidines, paraffin hydrocarbons, xylene, natural fats or waxes or Turkey red oil. Cf. *C. A.* **24**, 2639.

Apparatus for the manufacture of laminated rubber sheeting. ARCHIBALD C. BOWERS and WALTER E. HUMPHREY (to National Rubber Machinery Co.). U. S. 1,778,307, Oct. 14. Structural features.

Rubber solutions. F. KEMPTER. Brit. 330,953, Feb. 22, 1929. Rubber and solvent are stirred together in an app. such as a "paper ragging machine," in which the rubber is triturated between stirrers and irregularities on the wall of the app.

Rubber compositions. SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,778,707, Oct. 14. A polynitrophenyl ester of a substituted dithiocarbamic acid, such as 2,4-dinitrophenyldimethyl dithiocarbamate, is used as an accelerator in prepg. rubber compns. with a vulcanizing agent such as S and a metal oxide such as ZnO. U. S. 1,778,708 specifies the use of a phenylmethylenebisaliphatic substituted dithiocarbamate, such as phenylmethylenebisdimethyl dithiocarbamate. U. S. 1,778,709 specifies the use of a 2,6-dinitro-4-chlorophenyl ester of a substituted dithiocarbamic acid. Cf. *C. A.* **24**, 2638.

Rubber composition. IRVIN W. HUMPHREY (to Hercules Powder Co.). U. S. 1,776,857, Sept. 30. A compn. comprises rubber with rosin oil and rosin pitch (*e. g.*, 1–10% of decarboxylated rosin, which serves as a softening and blending agent).

Rubber tire-tread composition. R. E. JENKINSON (to Goodyear Tire & Rubber Co.). Brit. 330,282, Nov. 10, 1928. See U. S. 1,769,694 (*C. A.* **24**, 4665).

Rubber-coated fabric for tires, etc. GEORGE BAEKELAND (to Bakelite Corp.). U. S. 1,776,879, Sept. 30. A tire, belt, hose or similar article is formed with a rubber-coated fabric impregnated with a flexible resinoid such as one of the phenol-methylene type.

Mold with automatic temperature regulation for "electric-cured" tires. ALFRED A. GLIDDEN, THOMAS M. KNOWLAND and WARREN R. DOW (to Hood Rubber Co.). U. S. 1,777,486, Oct. 7.

Elastic tires. I. G. FARBENIND. A.-G. Fr. 36,406, Jan. 15, 1929. Addn. to 660,634 (*C. A.* **24**, 265). Elastic tires for wheels are made from products obtained by the polymerization of butadiene in the presence of rubber latex or substances resembling latex, with or without the addn. of natural or artificial resins and finely divided fillers such as lamp black.

"Age-resistant" rubber. CECIL J. T. CRONSHAW and WM. J. S. NAUNTON (to British Dyestuffs Corp., Ltd.). U. S. 1,777,352, Oct. 7. Acetaldehyde is condensed with a mixt. of equal parts of α- and β-naphthylamines in the presence of an acid condensing agent such as HCl; the product, after removal of the acid and isolation of the product, is added in small proportions (suitably about 1%) to a rubber mixt. before vulcanization.

Emulsions containing bitumen or oil and rubber. COLAS PRODUCTS, LTD., L. G. GABRIEL and J. F. BLOTT. Brit. 329,965, Feb. 27, 1929. Emulsions are prepd. by subjecting to agitation in a suitable mixer, such as a colloid mill, a mixt. of molten or liquid bitumen and rubber latex, or oil and rubber latex, without addn. of other dispersing agents. After the emulsification, a small quantity of a stabilizing agent such as an alkali caseinate may be added, or the emulsion may be coagulated to produce a vulcanizable mass. Details and examples are given.

Regeneration of old rubber. SOCIETÀ ITALIANA PIRELLI. Ger. 503,648, Oct. 14, 1926. The rubber is heated with an alk. soln. of av. concn. The amt. of alkali does not exceed the equiv. of the existing S and the mixing takes place at atm. pressure and at 200°. The app. is described.

Filtering material. FRANZ CLOUTH RHEINISCHE GUMMIWARENFABRIK A.-G. Ger. 505,207, May 3, 1928. Filaments or strips are prepd. from a rubber mix capable of yielding hard rubber when fully vulcanized. The filaments, etc., are partially vulcanized so that they remain elastic, then woven to form a sheet or the like and finally completely vulcanized.

Rubber substitute. ERNEST KLEIBER and PIERO GILARDI. Fr. 36,588, Feb. 26, 1929. See Brit. 312,741 (*C. A.* **24**, 990).

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 330,272, Dec. 29, 1928. "Diolefins such as isoprene or erythrene or 1,3-butadiene are polymerized by the emulsion process" in the presence of a salt of an org. base of high mol. wt. with an org. acid which is capable of emulsifying hydrocarbon material, such as the hydrochloride of diethylaminoethyloleylamide or of diethylaminoethoxyoleylanilide. Other active substances and emulsifying substances, etc., may be added.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 330,922, March 16, 1929. Polymerization products of butadiene and similar compds. which are insol. in C_6H_6 and which do not become plastic on the rollers are rendered sol. and plastic by treatment with an org. nitro compd. such as a nitrobenzene or dinitronaphthalene (suitably

by heating to about 150° and in the presence of a solvent or diluent). Several examples are given.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 36,424, Jan. 21, 1929. The quality of artificial rubber and like masses is improved by replacing the finely divided C of the parent patent by other substances of fine grain such as colloidal silicic acid or oxides of metals. Cf. *C. A.* **24**, 4425.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 36,590, Feb. 28, 1929. Addn. to 665,537. Artificial rubber is obtained by polymerizing 1,3-butadiene or its homologs or analogs to an unfinished state, mixing with more hydrocarbon and continuing the polymerization under the same or different conditions. Examples are given.

Checking deterioration of rubber. WM. S. CALCOTT, WM. A. DOUGLASS and MILES A. DAHLEN (to E. I. du Pont de Nemours & Co.). U. S. 1,778,548, Oct. 14. *p*-Hydroxydiphenyl ether, *p,p'*-dihydroxydiphenyl ether, 2,2'- or 3,3'-dihydroxydiphenyl ether, *o*-hydroxydiphenyl ether or other closely similar compds. are added in small proportion to rubber compns. before vulcanization. Cf. *C. A.* **23**, 4848.

Preventing deterioration of vulcanized rubber. CLAYTON W. BEDFORD (to B. F. Goodrich Co.). U. S. 1,777,634, Oct. 7. To check deterioration, there is incorporated in the material a product formed by the interaction of croton aldehyde and an amine such as $PhNH_2$ in the presence of an acid such as SO_2.

Rubber vulcanization accelerators. STANLEY J. PEACHEY. Fr. 685,655, Nov. 27, 1929. See Brit. 326,256 (*C. A.* **24**, 4426).

Vulcanizing rubber. SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,777,874, Oct. 7. There is added to the rubber a vulcanizing agent such as S, a metallic oxide such as ZnO, 2,4-dinitrophenyldimethyldithiocarbamate or similar compd., and an acid such as monochloroacetic acid capable of retarding the activity of the dithiocarbamate as a vulcanization accelerator; at the time of vulcanization, the latter may be facilitated by using also another stock contg. dibenzylamine.

Vulcanizing rubber. SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,777,960, Oct. 7. Rubber is combined with vulcanizing ingredients including S, a vulcanizing accelerator which is a deriv. of CS_2 such as the thiocarbonic acid disulfide of butanol, a metal compd. such as ZnO, and an amine such as *p*-toluidine (at least one of the materials being introduced by diffusion) and vulcanization is effected. Cf. *C. A.* **23**, 1309.

Vulcanizing rubber. WINFIELD SCOTT and WM. P. TER HORST (to Rubber Service Laboratories Co.). U. S. 1,777,737, Oct. 7. A mixt. of phenetidylguanidines (contg. approx. 70% of di-*p*-phenetidylguanidine) is used as an accelerator in vulcanizing with S. U. S. 1,777,738 (Winfield Scott to Rubber Service Lab. Co.) relates to the use as an accelerator of the reaction product of mercaptobenzothiazole and monophenylbiguanide.

Vulcanizing rubber. WINFIELD SCOTT. Ger. 503,647, Feb. 1, 1928. See Brit. 297,726 (*C. A.* **23**, 2851).

Vulcanizing rubber. W. A. MOORE (to Rubber Service Laboratories Co.). Brit. 330,981, Nov. 12, 1928. A rubber mixt. contg. S is vulcanized by heating it in water in which an insol. "ultraaccelerator" is suspended, such as the CS_2 derivs. of the reaction product of piperidine and CH_2O or similar compds.

Vulcanizing artificial rubber. I. G. FARBENIND. A.-G. Fr. 685,563, Aug. 29, 1929. Small quantities of Se in the presence of accelerators or S or both are used as a vulcanization agent in vulcanizing polymerization products of butadienes. Examples are given.

Apparatus for vulcanizing tires with transverse apertures in the tread. ANDREW J. FLEITER (to Lambert Tire & Rubber Co.). U. S. 1,778,071, Oct. 14. Structural features.

Press suitable for vulcanizing rubber belts, sheet packing, etc. ERNEST HOPKINSON (to New York Belting & Packing Co.). U. S. 1,777,310, Oct. 7. Structural features.

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The Influence of Zinc Oxide on the Action of the Principal Accelerators of Vulcanization*

The Preparation of Transparent Vulcanized Rubber

R. THIOLLET and G. MARTIN

IT HAS been known for a long time that the action of accelerators of vulcanization proceeds to a conclusion and in a regular way only in the presence of certain metallic oxides, of which zinc oxide is the most widely used. This substance behaves also as a reinforcing pigment, improving the physical properties of vulcanized rubber. We are not at the present time concerned with the second property, we are only concerned with ascertaining under what conditions zinc oxide promotes the action of accelerators.

Zinc oxide makes rubber opaque. With certain articles like molded nipples and vulcanized crepe soles, this opacity offers a serious inconvenience and we have studied how it is possible to obtain transparent vulcanizates.

To study these questions, we have carried out some vulcanization tests with the principal accelerators on the following three mixtures:

	I	II	III
Pale Crepe	100	100	100
Zinc Oxide	5	1	0
Palm Oil	1	1	1
Stearic Acid	0.5	0.5	0.5
Accelerator	..	..	..
Sulfur	..	..	..

*Translated from *Le Caoutchouc et le Gutta-percha*, Vol. 27, No. 317, pages 15084-7, July 15, 1930.

NAME OF ACCELERATOR	% of Sulfur on Rubber	% of Accelerator on rubber	Steam pressures corresponding to the characteristic temperature	T in min.
Zn isopropylxanthate	2	2	0	2
Zn methylphenyldithiocarbamate	1.8	0.7	1 kg.	24
Tetramethylthiuramdisulfide	1.8	0.4	2	8
Tetramethylthiurammonosulfide	1.8	0.4	2	8
Mercaptobenzothiazole	2.5	0.7	3	36
Diphenylguanidine	3	0.7	3	64
Di-o-tolylguanidine	3	0.6	3	56
Phenyltolylxylylguanidine	3	0.6	3	64
Triphenylguanidine	3.5	1	3	68
Ethylidene-aniline	3.5	1	2.5	40
Thiocarbanilide	5	2.5	3	88
Anhydroformaldehyde-aniline	4	2	3	72
Anhydroformaldehyde-p-toluidine	3.5	2	3	68
p-Nitrosodimethylaniline	3.5	1	2.8	60
Mercaptobenzothiazole / Diphenylguanidine	2.5	0.3 / 0.4	1.5	32
Mercaptobenzothiazole / Ethylidene-aniline	2.5	0.3 / 0.45	2	20
Zn methylphenyldithiocarbamate / Anhydroformaldehyde-aniline	1.8	0.7 / 1	1	24
Mercaptobenzothiazole / Anhydroformaldehyde-aniline	2.5	0.7 / 1	3	36

TABLE NO. 1

Choice of Conditions of Vulcanization.—The proportions of sulfur and of accelerator used correspond to those which are ordinarily used in practice.

Vulcanization was carried out at a characteristic temperature for a time, T, a little less than the time t corresponding at this temperature to the maximum vulcanization.

$$T \text{ is defined by } T = t - \frac{t}{5}$$

The characteristic temperatures and the corresponding times of maximum vulcanization were determined by the study we published in the October, 1929, number of *Le Caoutchouc et la Gutta-Percha.*

The accompanying table No. 1 summarizes the conditions under which the experiments were carried out.

On each of the mixtures thus prepared, tensile strength tests and accelerated aging tests were made.

Tensile Strength Tests.—Ring test pieces of definite dimensions were cut from each of the mixtures vulcanized under pressure. The mechanical properties were evaluated by the average of three dynamometer tests.

Aging Tests.—Samples such as we have just described were put in a ventilated oven, heated by an electric resistance, with a constant temperature control at 70°C. Every other day three samples of each mixture were withdrawn. Tensile strength tests were made after 24 hours' rest. The results represent the average of three tests. The total time of the aging test was ten days.

Results.—We have drawn the following conclusions from these tests:

1. Mixtures containing 5% of zinc oxide vulcanize in a normal way, but are opaque after vulcanization.

2. Mixtures vulcanized with 1% zinc oxide are in general transparent. Those vulcanized in the presence of accelerators composed of zinc salts of organic acids (Zn methylphenyldithiocarbamate; Zn isopropylxanthate) are not very transparent. In other mixtures containing accelerators which require relatively high proportions (guanidines) of sulfur, the transparency is masked by the sulfur "bloom." The physical properties of these mixtures are only slightly poorer than those of mixtures vulcanized in the presence of 5% zinc oxide. They age in the same way.

3. Certain accelerators can be vulcanized without zinc oxide.

The mixtures obtained in this way are transparent, the transparency being masked sometimes by a sulfur "bloom." However, the physical properties of mixtures so obtained are very much inferior to those of mixtures vulcanized in the presence of zinc oxide. Besides, the vulcanizates obtained age badly and become "tacky" after a few days in the oven.

At the same time a considerable diminution of their physical properties takes place.

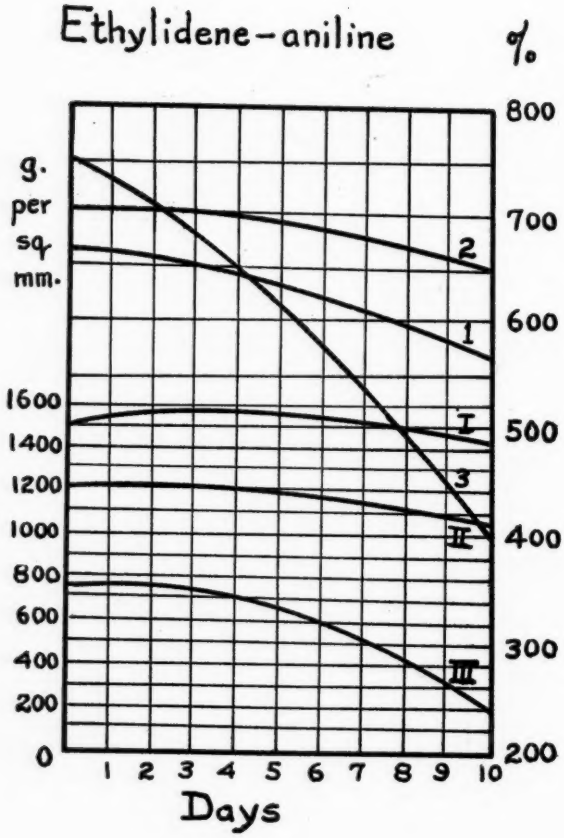
It is somewhat curious to learn that certain accelerators, like Zn methylphenyldithiocarbamate and mercaptobenzothiazole, which do not act without zinc oxide, become active if 1% of anhydroformaldehyde-aniline is added to the mixture. But the vulcanizates thus obtained also age badly.

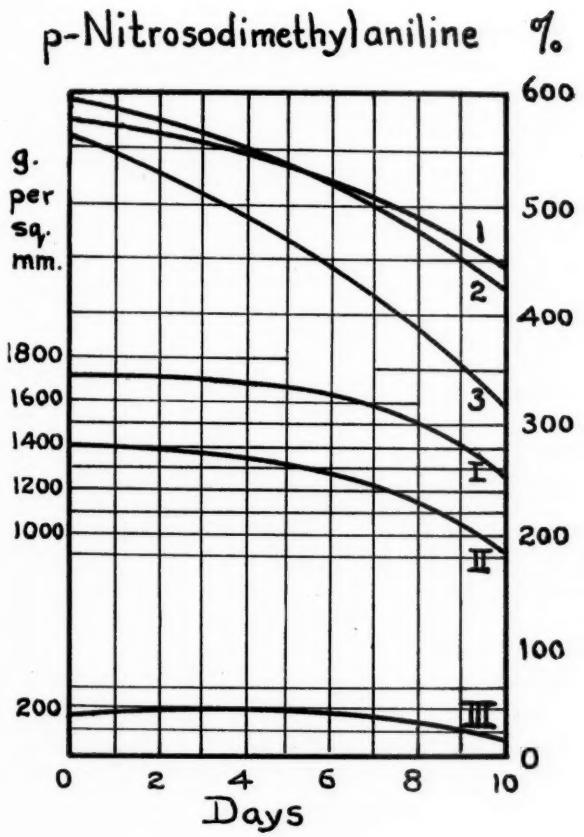
Ethylidene-aniline and *p*-nitrosodimethylaniline are the two substances which impart the best aging properties to mixtures. These properties are, however, very unsatisfactory from a practical point of view.

The accompanying graphs show the behavior on accelerated aging of mixtures vulcanized with and without zinc oxide and containing one or the other of these two accelerators.

In addition, these products give mixtures which are transparent but strongly colored. This makes ethylidene-aniline and *p*-nitrosodimethylaniline of little interest in the manufacture of transparent goods.

In the case of these two accelerators, the difference between the physical properties of mixtures containing 5% and 1% of zinc oxide is considerable. It is usually less for other accelerators.


Ethylidene-aniline
%
g. per sq mm.
800
700
600
500
400
300
200
1600
1400
1200
1000
800
600
400
200
0
2
1
I
3
II
III
1 2 3 4 5 6 7 8 9 10
Days


p-Nitrosodimethylaniline
%
600
500
400
300
200
100
0
g. per sq. mm.
1800
1600
1400
1200
1000
200
1
2
3
I
II
III
0
2
4
6
8
10
Days

PROPORTIONS OF ZINC OXIDE	5%			1%			0%		
Accelerator Used	Vulcanization	Bloom	Transparency	Vulcanization	Bloom	Transparency	Vulcanization	Bloom	Transparency
Zn isopropylxanthate	#	-	-	#	-	-	-	-	-
Zn methylphenyldithiocarbamate	#	-	-	#	-	-	-	-	-
Tetramethylthiuramdisulfide	#	-	-	#	-	#	-	-	-
Tetramethylthiurammonosulfide	#	-	-	#	#	#	-	-	-
Mercaptobenzothiazole	#	#	-	#	#	#	-	-	-
Diphenylguanidine	#	#	-	#	-	-	#	#	-
Di-o-tolylguanidine	#	#	-	#	-	-	#	#	-
Phenyltolylxylylguanidine	#	-	-	#	#	-	#	#	-
Triphenylguanidine	#	#	-	#	#	-	#	#	-
Ethylidene-aniline	#	-	-	#	-	#	#	-	#
Thiocarbanilide	#	#	-	#	#	#	-	-	-
Anhydroformaldehyde-aniline	#	#	-	#	#	#	-	-	-
Anhydroformaldehyde-p-toluidine	#	#	-	#	#	#	-	-	-
p-Nitrosodimethylaniline	#	-	-	#	-	#	-	-	-
Mercaptobenzothiazole + Diphenylguanidine	#	-	-	#	-	#	-	-	-
Mercaptobenzothiazole + Ethylidene-aniline	#	-	-	#	-	#	-	-	-
Zn methylphenyldithiocarbamate + Anhydroformaldehyde-aniline	#	-	-	#	-	#	-	-	#
Mercaptobenzothiazole + Anhydroformaldehyde-aniline	#	-	-	#	-	#	-	-	#

EXPLANATION OF SIGNS :

Vulcanization : # vulcanised; - did not vulcanise

"Bloom" : # sulfur "bloom"; - no sulfur "bloom"

Transparency : # mixture transparent; - mixture opaque

TABLE NO. 2

Table No. 2 shows the behavior of the different accelerators in the presence of 5% and 1% of zinc oxide, and also in its absence.

Conclusions.—The results of the data in the accompanying table show that it is necessary to use zinc oxide with all the accelerators of vulcanization. The proportion of this adjuvant, generally fixed at 5%, can be reduced to 1% in the case of certain accelerators, and this will give transparent mixtures. It is naturally well to

select accelerators which do not color the rubber noticeably and which allow vulcanization with such a small proportion of sulfur that "blooming" does not occur.

The formulas indicated below are well adapted to the preparation of transparent mixtures.

Pale crepe	100	100	100	100
Zinc oxide	1	1	1	1
Palm oil	1	1	1	1
Stearic acid	0.5	0.5	0.5	0.5
Sulfur	1.8	1.8	2.5	2.5
Tetramethylthiuramdisulfide	0.4	..	..	..
Tetramethylthiurammonosulfide ..	..	0.4	..	..
Mercaptobenzothiazole	..	..	0.7	0.3
Diphenylguanidine	..	..	..	0.4
Vulcanization, time in min.....	8	8	35	30
Steam Pressure in kg.....	2	2	3	1.5

[Reprinted from THE RUBBER AGE (N. Y.), Vol. 28, No. 4, Nov. 25, 1930]

The Viscosity of Rubber Solutions under Influence of Benzoyl Peroxide*

A Contribution to Methods for Determining Inorganic Fillers, Etc., in Rubber Mixtures

G. FROMANDI

IN THE determination of mineral and certain organic substances in rubber mixtures by the aid of disintegration with paraffin oil or anisol, difficulties occur during filtration in the presence of golden antimony which require the use of a centrifuge, since the relatively high viscosity of the colloid system does not permit a sufficiently high rate of sedimentation for practical purposes. Some investigations of rubber mixtures containing golden antimony, in which for certain reasons the use of a centrifuge was impracticable, necessitated the development of a method which would obviate the use of a centrifuge. By means of decalin (decahydronaphthalene) and benzoyl peroxide it was possible to so control the ordinary disintegration that the sedimentation of the filler and antimony particles increased to such an extent that filtration was no longer difficult.

The method[1] is as follows:—The material, which has been prepared as usual (about 1 g. of the original sample), is placed in a weighed, wide-necked Erlenmeyer flask of about 300 cc. provided with an air condenser and is covered with 40 cc. of decalin of

*Presented before the Deutsche Kautschuk Gesellschaft, Frankfort-am-Main, June, 1930. Translated from Kautschuk.

boiling point 191° C. (the required quantity of which should be especially purified by distillation at the time). It is heated at boiling temperature until the rubber substance is almost completely dissolved, according to the composition of the mixture, the time required being from four to eight hours[2]. To the mixture 1-1.5 g. of "purest" benzoyl peroxide is added, and it is boiled from one to two hours more until the brown coloration of the golden antimony appears. After cooling, the flask is almost wholly filled with petroleum ether (having a low boiling point), and is allowed to stand until the precipitate is settled out. After twenty-four hours at the most separation is complete and the usual subsequent treatment can be carried out without difficulty, for which a porcelain or glass filter cup with not too coarse a filter plate is found advantageous. The precipitate in most cases rests so firmly on the bottom that the clear liquid above can easily be removed quantitatively by thorough decanting.

This method is suited not only for vulcanizates containing golden antimony but also quite generally for the determination of inorganic fillers in rubber compounds. The chemistry of the action of benzoyl peroxide on these systems may probably be explained by the fact that benzoyl peroxide undergoes decomposition under the influence of high temperatures, resulting in the formation of a new hydrocarbon or of diphenyl benzoate, biphenyl and oxygen which acts directly on the double and molecular compounds still present, splitting the sulphur bridges and probably has a disaggregating effect as well. This results in a relatively great diminution of viscosity, which approaches a value scarcely different from the pure solvent.

In connection with the method developed, the influence of benzoyl peroxide on a solution of rubber in benzene was investigated more closely, and in the investigation it was assumed that decalin as such does not influence the degree of polymerization or of aggregation of the dissolved rubber to any essential degree, and as a result can be replaced by benzene.

The system used in this series of experiments consisted of a solution of 1 g. of rubber or of 1 g. of rubber + 1 g. of benzoyl peroxide in 100 cc. of benzene, and was studied viscosimetrically under the following physical conditions:—

A Peroxide-free solution in the dark
A' Peroxide-free solution in diffused daylight
B Solution containing peroxide in the dark
B' Solution containing peroxide in diffused daylight
A" Peroxide-free solution in diffused daylight heated to 80°
B" Solution containing peroxide in diffused daylight heated to 80°

The first latex crepe, which had an acetone-soluble content of 2.84%, was dissolved in benzene after a twelve hour extraction with acetone. After the small quantity of impurities had settled out, it was filtered through glass wool and then through wadding with the most careful exclusion of light and air, precipitated by the careful addition of acetone, and dried *in vacuo* at 50° to constant weight. The benzene solution thus obtained was entirely clear and practically colorless. The Ostwald viscosimeter used had a capillary

diameter of 1 mm., the quantity of liquid amounted to 2 cc.[3] and the temperature of the bath was 25°±0.2° C. Since the measurements were only relative, the time of passage of the flow was measured only in seconds.

The influence of benzoyl peroxide on the rubber benzene solution (which contained both 1 per cent of rubber and 1 per cent of benzoyl peroxide) under varying physical conditions led to a relatively great depression in the viscosity, which the following curves show in relation to the time of treatment (See Figure 1).

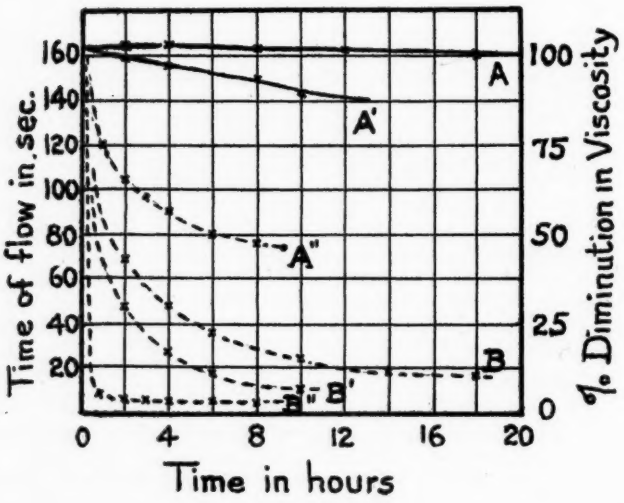


Figure 1

Influence of benzoyl peroxide on the viscosity of a 1 per cent. solution of rubber in benzene under different physical conditions

The form of the curves show that benzoyl peroxide reduces the viscosity of the solution to a marked degree. The different relations between the diminuation in viscosity and the time according to the nature of the physical conditions and the tendency for these relations to approach definite values which are markedly different are also characteristic of the system. Heating at 80° C. in daylight caused even after one hour an increase in viscosity of about 95 per cent, in the dark of 91 per cent, of the original value of the solution, while the peroxide-free solution after the same time underwent a diminution of only 26 per cent. On standing in diffused daylight the corresponding values were 58 and 2 per cent, respectively. Similar results were obtained in the dark. The numerical difference in the viscosities compared with those of solutions under the influence of diffused daylight is relatively small, showing that this factor plays only a secondary part in the influence of benzoyl peroxide on rubber solutions.

Because of its high sensitivity, determinations of the viscosity

of the peroxide-free solution as a function of time over a period of one day, or 8 to 10 hours, leads to relatively great divergences of the individual experimental measurements, since "diffuse daylight" is subject to continuous variations. It is recommended therefore that in such cases all measurements be made under the most nearly comparable conditions on the same day, so that variations in the results are minimized as much as possible.

Similar results were obtained with direct sunlight, where the samples were exposed on the roof of the laboratory. Table I shows the influence of direct sunlight on the viscosity.

Table 1

The Viscosity of a 1 Per Cent Rubber-Benzoyl Peroxide Solution under the Influence of Direct Sunlight.

Exposure to light in days	Time of passage of flow of solution in seconds		Diminution of viscosity of Solution in per cent	
	Peroxide-free	*Containing Peroxide*	*Peroxide-free*	*Containing Peroxide*
0	163.5	—	—	—
1	94.5	8.6	42	95
3	61.5	5.3	62	97

Direct sunlight causes a great decrease in the viscosity of both solutions, and this diminution during the one day's exposure is numerically about the same as the diminution which was obtained by heating for eight days at 80° C., and is distinguished from the latter only by its rate.

An investigation which is closely related to that above and which deals with the behavior of both solutions under the influence of ultra-violet light[4] (analytical quartz lamp of Heräus-Hanau) gave the results in Table 2[5]. The experimental equipment consisted of a graduated quartz test tube containing the solution, which was placed about 21 cm. from the burner whose light by the insertion of a black glass filter corresponded to a wave length of 366$\mu\mu$. A current of oxygen-free hydrogen was slowly passed through the solution in order to keep away the atmospheric oxygen as well as the ozone which was formed under the influence of the ultra violet rays, and in order at the same time to keep the surface renewed at all times. To determine the viscosity, 2 cc. were removed and after the measurements they were returned, while the loss of solvent by the gas stream was replenished. The temperature averaged 22° C.

The table shows that the diminution in viscosity of both the radiated solutions approaches both in its magnitude and in its dependence upon the time that obtained by warming and secondly the table shows that the action of benzoyl peroxide on rubber in solution under the influence of ultra-violet rays undergoes a considerable acceleration.

In the reaction system which was thus studied under different physical conditions, the lowering of the viscosity was probably above all a result of an attack by the benzoyl peroxide on the double or molecular bonds of the rubber and also a result of its state of aggregation. At elevated temperatures the first factor probably

Table 2

The Action of Ultra-Violet Rays on the Viscosity of a 1 Per Cent Rubber-Benzene Solution, (a) Peroxide-free and (b) Containing Peroxide.

Exposure in hours	Time of flow in sec. of Solution		Diminution of the Solution in per cent	
	Peroxide-free Solution	*Containing Peroxide*	*Peroxide-free*	*Containing Peroxide*
0	163.5	—	—	—
1	84.9	16.8	48	90
2	60.7	10.0	63	94
4	46.7	7.2	72	95
6	36.8	6.0	77	96

predominates, which would explain the numerical difference in the viscosimetric data compared with the measurements at room temperature. The form or the course of the viscosity curves is to be regarded as a measure of the rate of oxidation and of disaggregation.

Benzoyl peroxide, which is used at the present day more and more for bleaching oils, fats, waxes and resins, according to Ostromislensky[6], is a substance which is capable of vulcanizing rubber in the absence of sulphur, and which in the presence of sulphur plays the part of a vulcanizing agent. Whether these peroxide vulcanizates can be regarded as identical with sulphur vulcanizates in their essential physical and chemical characteristics or merely as pseudo-vulcanizates must remain uncertain for the present time. Experiments in this field, which may be considered as a contribution to the problem of vulcanization in general, are however in progress, and will be reported in a later publication.

References

[1]Cf. the method of Scott for the determination of fibrous and other mechanical impurities in unvulcanized rubber, *India Rubber J.* **79**, 158 (1930).

[2]In the presence of certain kinds of reclaimed rubber the heating must be prolonged.

[3]The viscosity curve for the solution containing peroxide which was heated at 80° in darkness coincided so closely with the curve of the corresponding irradiated solution that the slight numerical differences can from a practical point of view be disregarded.

[4]According to Scheibe and Pummerer [cf. *Ber.* **60**, 2163 (1927)] rubber absorbs only below approximately 230$\mu\mu$, with a maximum around 200$\mu\mu$.

[5]The measurements are naturally of a more or less exploring character, since the position of the absorption range of benzene does not permit of an unequivocal conclusion.

[6]*India Rubber World*, Vol. **80**, Dec., 1929, p. 55, in which article references to earlier literature are cited.

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Standardization of Ozone Testing*

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THE FISK RUBBER COMPANY

THE progressive deterioration of soft vulcanized rubber, proceeding independently of actual wear, has always been a source of annoyance to the trade. Although evidences of such deterioration are varied in character, the many forms may be conveniently classified as surface deterioration and deterioration throughout the rubber.

Surface deterioration, characterized by superficial film formation, is greatly accelerated when vulcanized rubber is exposed to light, particularly rays of short wave length, but that this function of light in the destruction of rubber is indirect in operation was recognized as early as 1883, by Burhardt (*Jour. Soc. Chem. Ind.* 2, 119, 1883). The agency responsible for the changes which rubber undergoes on exposure to the atmosphere is undoubtedly oxygen, and suggested by Spiller (*Jour. Chem. Soc.* [London] 18, 44, 1865), as far back as 1865. That oxygen is essential for the deterioration of rubber has been shown by Fickenday (*Kolloid Ztg.* 9, 81, 1911), and many others since. The effect of sunlight on either raw or vulcanized rubber, is believed by Henri (*Caout. et Gutta Percha* 7, 2848, 1909) to be analogous, although Peachy and Leon (*Jour. Soc. Chem. Ind.* 37, 56T, 1918) offer the opinion that vulcanized rubber oxidizes less rapidly than raw rubber. Later investigators have proceeded still further in their conclusions, and Tuttle (*The Rubber Age,* N. Y. 8, 271-2, 1921) states, after studying the acetone solubility curves of vulcanized rubber exposed to light, that the action of the latter is one of oxidation, which when once started proceeds rapidly, due to the catalyzing effect of small amounts of oxidized rubber so formed.

That oxidation may be a secondary effect of light is entirely

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EDITOR'S NOTE: Since the delivery of this paper the author has severed his connections with the Fisk Rubber Company and is at present associated with the United Carbon Company, Charleston, W. Va.

possible, and Whitby (*Plantation and Rubber Testing*, 1920) and van Rossem (*India Rubber Journal* 48, 172, 1914) are of the opinion that oxidation is preceded by certain physical changes. This point is further substantiated by the findings of Asano (*India Rubber Journal* 70, 9, 352, 1925), who was able to produce benzol insoluble products by exposing raw rubber to the action of ultraviolet light, even when the samples were enveloped in inert gas, and concludes that oxidation is a secondary effect following an individual action exerted by the ultraviolet rays themselves.

An extremely interesting phenomenon associated with the film formation already referred to, is the so-called "sun-checking" or "sun-cracking" which results from exposing vulcanized rubber under tension to the action of sunlight, and probably due to the decreased elasticity of the oxidation products constituting the film formation, with consequent cracking under the tension present.

Williams (*Ind. Eng. Chem.* 18, 4, 369, 1926) has offered experimental evidence indicating the presence of ozone as necessary for the production of this cracking, the probability of which was previously suggested by Haushalter (*India Rubber Journal* 70, 20, 897, 1925), in his publication on the measurement of the effect of corona on rubber subjected to high voltages, and Peritor (*Gummi Ztg.* 40, 95, 1925), who goes so far as to suggest the use of ozone as a testing agency for rubber deterioration.

The apparent greater tendency of vulcanized rubber to crack under exposure to ozone, when maintained at a definite degree of elongation, has been noted by Shepard, Krall and Morris (*Ind. Eng. Chem.* 18, 6, 615, 1926), and Somerville *et al* (*The Rubber Age* [N. Y], Dec. 10, 1929), in investigating the effect of aging rubber under varying elongations, found that the effect of ozone and sunlight were analogous, and emphasized the point that an elongation of 5% to 10% of the rubber constituted a critical stretch at which maximum cracking resulted on exposure of vulcanized rubber to either of these agencies.

It has been the purpose of the present investigation to expand on the reported observations by studying the various factors which influence the degree and type of cracking produced on exposing vulcanized rubber under tension to the action of ozone, and by systematic correlation of the results obtained, to develop a standardized technic for the ozone testing of rubber products.

Apparatus and Method

A constant source of ozone, as regards concentration and volume, is obviously a prime requisite if consistent results are to be obtained, and in the choice of apparatus for this work, adequate control of the factors governing the rate of ozone generation, i.e., humidity of the air supplied to, and temperature of the ozonizing chamber, were carefully considered.

The ozonizer proper is a modification of the apparatus described by Smith (*Jour. Am. Chem. Soc.* 47, 7, 1844, 1925), consisting of a Berthelot tube A. (Figure 1.), the inner electrode being formed of mercury, and the outer electrode by wrapping the external tube with tinfoil and protecting with a thick coat of beeswax. The tension between the electrodes (5.000-17,000 V.), is furnished and

regulated by means of a 0.5 k.v.a. autotransformer. The temperature of the ozonizing chamber can be regulated to within 1° C. by means of a water bath B. which entirely surrounds the ozonizer. The air to the ozonizer is dried by passing through columns of calcium chloride E., sulphuric acid F., and glass wool G., and its rate of flow is measured and controlled by flowmeter D. Proper dilution of the ozonized air to the desired concentration is accomplished in a mixing bottle I., by means of air introduced through flowmeter H. From this point it is supplied to the testing chamber J., where it is kept in constant circulation by the fan K.

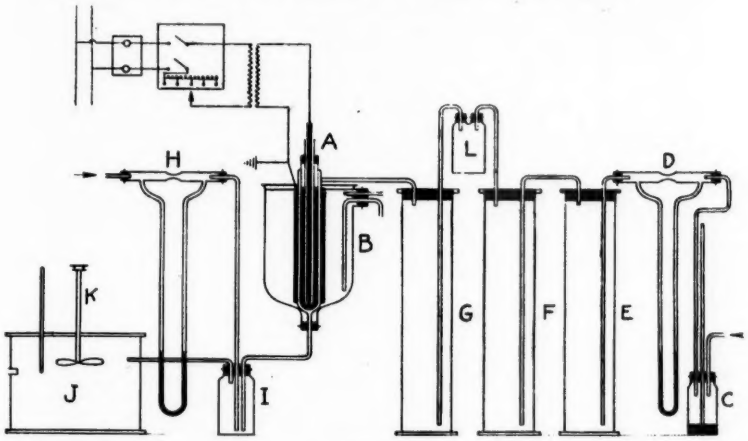


Figure 1

The specimens of rubber to be exposed consist of strips 3″ x 0.5″ x 0.1″, on which a longitudinal section 1″ in length is accurately marked. The strip is laid flat on a board, one end fastened, the desired elongation obtained by stretching until the 1″ section assumes the proper proportions, and the opposite end secured. All observations were confined to the 1″ section, the percentage elongation of which could be accurately determined.

The concentration of the ozone being supplied to the exposure chamber was constantly checked, the method employed being that described by McDonnel (*Ind. Eng. Chem.* 18, 2, 135, 1926), in which the ozonized air is bubbled through potassium iodide and starch solutions, to which sodium thiosulphate has been added in amount equivalent to a definite and suitable iodine standard. When the iodine liberated by the ozone from the potassium iodide solution exceeds the reactive limit of the sodium thiosulphate, the starch indicator turns blue, and from the time required for the completion of the reaction and the volume of ozonized air bubbled through, the concentration is determined. Preliminary work indicated a dilution of 1; 50,000 to be best suited for comparative purposes after an exposure of 30 minutes, and was the dilution adopted for the entire work reported in this paper, except of course, where the effect of varying the concentration was being observed. The exposure period selected was 30 minutes and was used for all tests.

Experimental Part

In studying the effect of fundamental variables, a pure gum stock was used composed of rubber-100, sulphur-3, zinc oxide-5, and Captax 0.5. The influence of compounding ingredients was investigated on the same stock to which had been added 10, 20 and 30 volumes on the rubber of zinc oxide, carbon black and natural ground whiting.

A cure just below the optimum was selected as best serving the purpose of the work, and was employed in all cases excepting where the effect of the state of cure was under observation.

The term maximum cracking, where used for the purpose of description in this report, implies the first point in a series of elongations at which the surface of the sample under examination was entirely covered with cracks (see Figure 2).

All series were allowed 72 hours stretch period before exposing them to ozone, for reasons which will be discussed under the effect of varying the stretch period.

For the purpose of comparison, all strips were uniformly stretched to 100% after the exposure period, and the series illustrated in this paper were photographed at this elongation.

Effect of Varying Elongation

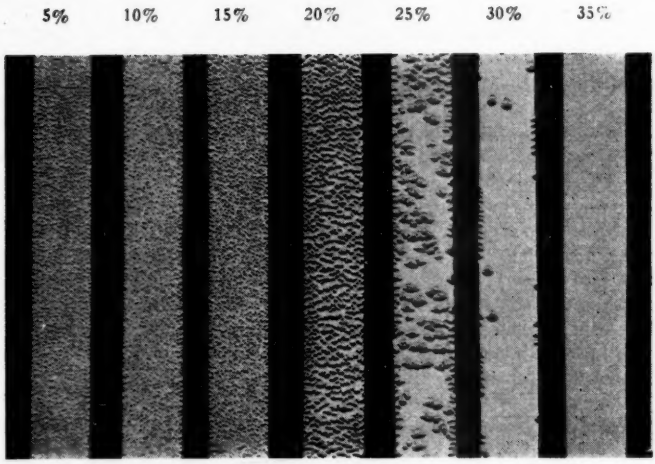
The apparent tendency of ozone to exert its greatest activity on vulcanized rubber at certain elongations, reported in the literature by several observers, was studied by exposing series of various stocks, representing a range of stretch from 0 to 100%. The results obtained indicated the influence of elongating rubber on its reaction to exposure to ozone to be of a dual nature. First, the greater the elongation employed, the smaller became the dimensions of the individual cracks, and secondly, the number of cracks resulting from the exposure increased proportionally to the degree of elongation up to a point of maximum cracking, which in the case of a pure gum stock occurred at 10% elongation.

The elongation of maximum cracking, or "critical elongation," varied for different types of stocks, a point also observed by Kelly, Taylor and Jones (*Ind. Eng. Chem.* 20, 3, 296, 1928), in connection with their study of sunlight aging and will be referred to again under the effect of compounding.

Effect of Varying Stretch Period Before Exposure

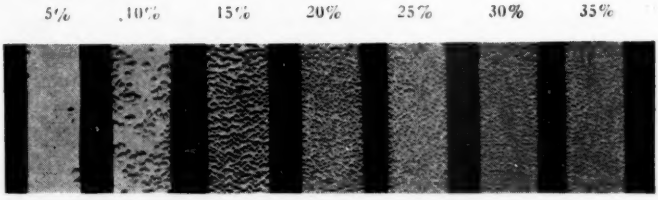
Early in this work, it became apparent that the stretch period to which a stock was subjected before its exposure to ozone, had a marked influence in determining the degree of elongation at which maximum cracking was produced. When a series of progressive elongations of rubber stock was given increasing periods of stretch, from 1 minute to 120 hours, before exposure, the point of maximum cracking evidenced a decided shift in the direction of higher elongation. This was particularly noticeable in the instance of a highly compounded stock, and quite slight in the case of pure gum stock.

Indications were that this shift is proportional to the duration of the stretch period up to 72 hours, at which time equilibrium was

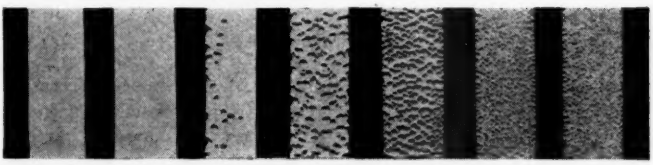


Maximum Cracking at 20%

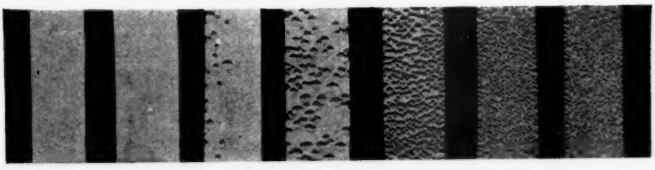
Figure 2



Exposure Immediately After Stretch



Exposure After 72 Hours Stretch



Exposure After 120 Hours Stretch

Figure 3

established regardless of the extent of the compounding (Figure 3).

This observation substantiates the findings of Haushalter, Jones and Schade (*Ind. Eng. Chem.* 20, 3, 300, 1928) that the degree of cracking obtained is dependent on the stresses existing in a stock rather than its elongation, all other conditions being equal. Increasing the duration of the stretch period correspondingly increases the permanent set, resulting in decreased tension existing although the elongation may remain the same, a point also noted by Balazo (*Gummi Ztg.* 43, 708, 710). This decrease in tension, termed "tension loss" by Ariano (*Il Nuovo Cimento,* March, 1929), continues until equilibrium is established, when the stresses existing at an arbitrary elongation correspond to those which existed originally at a lower elongation. Hence, if 15% represents the critical elongation when a sample is exposed immediately after stretch this point will have shifted to a decidedly higher elongation when subjected to 72 hours under tension before exposure.

Effect of Ozone Concentration and Duration of Exposure

Exposing a series of rubber compounds to the action of different concentrations of ozone, under varying degrees of stretch, showed that the type and number of cracks produced at a given elongation, were not materially affected by the concentration used. The intensity of the individual cracks was, however, greatly increased proportional to the concentration of ozone, and the length of exposure required for the production of a given degree of cracking was correspondingly reduced.

Increasing the exposure period, the concentration of the ozone remaining the same, gave similar results (Figure 4).

Effect of State of Cure

For the purpose of investigating the role played by the state of cure existing in a stock, in its susceptibility to cracking on exposure to ozone, a series representing a range of cures from zero to a decided overcure was tested at a predetermined elongation critical for the stock used.

The results obtained indicated that overcure when compared with the proper cure, had little influence on the extent of cracking produced. There did exist, however, a slight tendency to greater intensity of cracking in the overcured samples, which is in agreement with the findings of Krahl (*Kautschuk* 159-60, 180-3, 1927).

Undercured samples exhibited less cracking, especially as the state of no cure was approached. This is probably due to the greater mobility which exists in the lower cures, with consequent increased accommodation to the tension applied resulting in decreased internal stresses and less resistance to the stretch applied being developed, than in higher cures at the same elongation.

Effect of Temperature

Comparative tests carried out at increased temperatures, evidenced a slight shift to have taken place in the point of maximum cracking toward lower elongation. Also, the time of exposure necessary to produce a given degree of cracking was materially

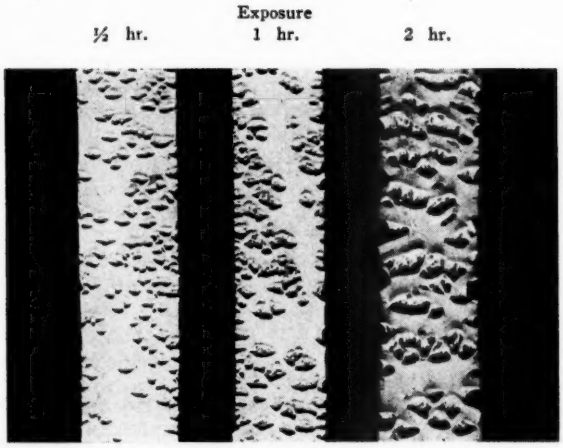
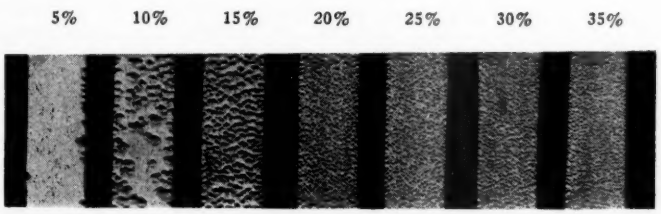
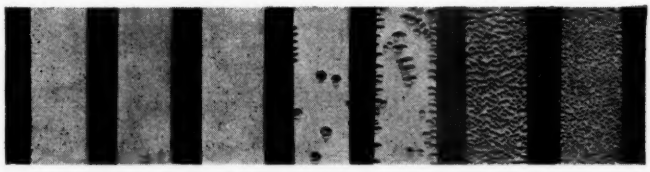


Figure 4



10 Volumes Filler

20 Volumes Filler



30 Volumes Filler

Figure 5

reduced. A series exposed at 160°F. required about half the exposure necessary to produce similar intensity of cracking at 60°F.

The observed shift in the critical elongation is undoubtedly due to the tendency of vulcanized rubber to contract when subjected to increased temperatures (Joule Effect), which according to Williams (*Ind. Eng. Chem.* 21, 9, 872, 1929), increases its resistance to strain, thus creating additional stresses.

It is natural to expect an increased activity of the ozone at higher temperatures, but no doubt the reaction is accelerated by the more receptive surface which results from the depolymerization products formed.

Freezing vulcanized rubber, as was anticipated, produced an effect directly opposite to that obtained by heating. Series of elongations of both pure gum and compounded stocks, when embedded in CO_2 snow, with one surface only exposed, for half an hour before and during the ozone test period, gave no indication of cracking even after several hours' exposure to increased concentrations of ozone. On allowing such samples to return to room temperature, however, and again exposing them, cracking resulted in a normal manner except that the critical elongation shifted to a slightly higher position in the series. Similar treatment of stocks at somewhat higher temperatures but below 0°C., while not entirely eliminating ozone cracking showed the latter to have been retarded considerably, a decided influence being exerted on the critical elongation, which experienced a progressive shift in the direction of higher elongation commensurate with the degree of cold at which the test was conducted.

Effect of Humidity

Conducting tests at varying degrees of humidity had no noticeable effect on the results obtained. Neither the type nor the intensity of the cracks produced were effected to a visible extent, and the critical elongation remained constant. It is quite probable, however, that the conditions reported by the Physical Testing Committee of the Rubber Division, A. C. S. (*Ind. Eng. Chem.* 20, 11, 1245, 1928), regarding the effect of humidity changes on the physical properties of vulcanized rubber, maintain for this method of aging although external manifestations were too slight to be observed.

Effect of Compounding

As mentioned earlier in this paper, the critical elongation of any stock depends on the tension present, and to what extent this tension exceeds the breaking stress of the superficial film produced by the exposure to ozone. This tension is governed by the stretch applied and the permanent set of the stock. Since varying amount of compounding ingredients has been shown by North (*India Rubber World* 63, 98, 1920) to materially affect the permanent set, it is natural that such variations should also influence the critical elongation of a rubber stock. The accuracy of this assumption was demonstrated by observing the effect of ozone on three stocks containing 10, 20 and 30 volumes of zinc oxide, respectively. Comparison of the results obtained showed a considerable shift in the critical elongation to occur in the direction of increased stretch, and proportional to the loading of zinc oxide employed. For 10 volumes of filler the critical elongation was located at 15% stretch, which point had

shifted to 20% when the zinc oxide was increased to 20 volumes, with a further shift to 30% stretch when 30 volumes of the filler were used (Figure 5).

Vogt and Evans (*Ind. Eng. Chem.* 15, 1015, 1923), in studying the effect of fillers on the properties of rubber stocks, classified them into two groups, depending on whether they were productive of isotropic or anisotropic physical characteristics, when the stocks into which they were incorporated were tested in different directions. Considering these classes separately, they found that the smaller the particle size the greater was the permanent set when the same volume loading was employed. To demonstrate the application of this observation as a determinant of the critical elongation in the ozone testing of rubber stocks, three stocks containing 10, 20 and 30 volumes on the rubber of whiting, zinc oxide and carbon black were exposed in series to ozone. These ingredients represent a wide range of particle size, being approximately 5.0μ, 0.5μ and 0.1μ, respectively. As it was impossible to adequately illustrate by means of photographs the comparative results obtained, they are offered in tabulated form.

		Critical Elongation		
Filler	**Particle Size**	**10 *Volumes Loading***	**20 *Volumes Loading***	**30 *Volumes Loading***
Whiting	5.0μ	10%	12%	15%
Zinc Oxide	0.5μ	15%	20%	30%
Carbon Black	0.1μ	20%	35%	50%

It will be noticed that as the particle size of the filler decreases, the elongation at which maximum cracking occurs is increased. This effect may be explained on the basis of permanent set, which, increasing proportional to the total surface area of the filler particles, exerts a correspondingly neutralizing effect on the tension produced by elongation to a given stretch, requiring the degree of elongation necessary for the development of a definite tension to be increased with the volume loading.

Discussion

The very low tensile strength of the film produced by ozone on the surface of rubber under tension, apparently offers the best explanation for the cracking phenomenon associated with it. As compared with rubber, this film has an extremely low breaking stress, with the result that in some cases an elongation of 5% to 10% in the rubber, is sufficient to develop a tension exceeding this breaking stress. At this point cracking of the film proceeds until the tension is reduced below this limit. That the number of cracks produced per unit area depends on the extent to which the tension present exceeds the breaking stress of the film, is well illustrated by the results obtained by varying the elongation of the rubber during its exposure to ozone. In the lower elongation, where the tension only slightly exceeds the breaking stress, the number of cracks appearing

were few, while in the higher elongations in which greatly excessive tensions were developed, the cracking became so extensive as to, in some cases, cover the entire surface of the rubber.

The observed variations in magnitude of the individual cracks, when considered from the results obtained using increasing concentrations of ozone, appear to be controlled by the thickness of the film formed. Of the factors investigated, high concentrations of ozone, increased temperature during exposure, and increased exposure periods, all of which may be expected to increase the thickness of the resulting film, invariably exhibited a marked influence on the dimensions of the individual cracks, being enlarged in each case. It is quite interesting to note, that the introduction of carbon black into a rubber compound produces similar, even if less pronounced effect. No explanation of this point is offered, but the high absorptive capacity of the carbon black suggests a possible solution.

The close relationship between the tension present in the rubber and the degree of cracking developed superficially by ozone, obviously implies that conditions productive of stress-strain changes will indirectly control the extent of cracking exhibited by any one stock. The variations observed when the duration of the stretch period before exposure is increased, must, therefore, be explained as resulting from the changes taking place in the stress-strain relationship during the stretch. Such changes will cease when equilibrium has been established between the plastic and elastic properties of the rubber, which for all stocks studied up to an elongation of 100%, a stretch period of 72 hours proved sufficient.

The influence of fillers has an important bearing on the number of cracks per unit area that will be produced at a given elongation. That the stress-strain relationship of a rubber stock is considerably affected by the particle size and extent of loading has been shown, and the application of this effect in compounding may offer a new point of attack on the problem of retarding ozone cracking. When the range of stretch to which rubber is likely to be subjected during service is known, it seems quite possible that by proper compounding the tension that will be developed by the rubber within the range of stretch so determined, could be controlled so as to assure a minimum if not complete elimination of cracking during its subsequent exposure during service to atmospheric conditions. Since the paraffin treatment of rubber as a protective measure against oxidation was patented by Kreusler and Budde (*D. R. P.* 18, 740, Aug. 26, 1881), it has been customary to combat the problem of surface cracking by the introduction of ingredients, which by virtue of their tendency to bloom out to the surface afford a certain amount of protection to the rubber. Experience indicates such protection may be quite temporary, and products so treated when placed in service likely to cause the rubber surface to be robbed of its protective coating, by abrasion or otherwise, show the efficiency of this procedure to decrease rapidly.

The retarding of cracking by control of the tension developed at a specified elongation through the medium of suitable compounding, if and when possible, should be permanent, which point the author considers of sufficient importance to merit further investigation. Preliminary studies along this line have been quite encouraging and additional observations are contemplated.

Summarizing, the results obtained in the course of the present investigation indicate that when the factors which tend to influence the activity of ozone on rubber under tension are adequately controlled, consistent and comparable results may be obtained. That these results are sufficiently significant to evaluate the ozone retarding properties of individual stocks, and the usefulness of the various ozone resisting compounding materials. A new angle of attack on the problem of elimination of ozone cracking has been suggested, which may be productive of permanent relief. The necessity of further work along such lines, and the correlation of the results obtained by this method of aging and that occurring naturally is emphasized, and it is expected that this work will be continued and reported in the future.

Acknowledgment

The writer wishes to express his sincere thanks to E. W. Fuller for the kind interest and assistance extended during the preparation of this paper.

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Overflow During Vulcanization*

Its Dependence Upon Inactive and Active Fillers, and Errors in Previous Calculations of the Specific Gravity of Vulcanizates Resulting from It

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THE overflow which takes place with every rubber mixture during vulcanization, if it is vulcanized in a mold, is a source of trouble to the rubber manufacturers and is therefore a problem of the greatest economic importance in rubber technology. If raw rubber to which nothing has been added is exposed to vulcanization conditions it becomes soft but does not increase in volume in any way. Quite a different result is obtained if a sulfur-rubber mixture is vulcanized in the conventional way or if an inactive or active filler is added to this rubber-sulfur mixture. In fact, it may be said in general that every case of a vulcanizate with sulfur is associated with an increase in volume.

In connection with an explanation of the overflow the following questions arose:

1. In what way do inactive fillers affect overflow?
2. In what way does an increase of a given inactive filler influence the overflow?
3. Do different inactive fillers influence the overflow in the same way?
4. In what way do active fillers influence the overflow?

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5. In what way does an increase of a given active filler influence the overflow?

6. Do different active fillers influence the overflow in the same way?

First to be considered was the overflow of a rubber-sulfur-zinc oxide-accelerator-base mixture prepared in the following way:

Base Mix		Specific Gravity	Volume
Smoked Sheets	10.0 g.	0.89	11.236
Sulfur	0.3 g.	2.07	0.144
Zn oxide	0.5 g.	5.42	0.092
Mercaptobenzothiazole	0.1 g.	1.42	0.070
	10.9 g.		11.542

A ball of 2 cm. diam., *i. e.*, having a volume of 4.1888 cc., was made from this mixture. The calculated specific gravity of the mixture was 0.944, the weight of the unvulcanized ball was 3.98 g., a greater precision was not obtainable.

This, as well as the subsequent vulcanizations, were carried out in a press, thus:

10 min. increase to 143° C.
30 min. at 143° C.

After vulcanization the overflow was carefully cut off and the ball and overflow were weighed:

Weight of ball before vulcanization (the ball was fitted to the mold carefully)	3.98 g.
Weight of ball after vulcanization.....	3.78 g.
Overflow	0.20 g.
Overflow of base mixture.....	5.02%

The ball of the base mixture gave under a load of 1 kg. in the Ditmar ball pressure apparatus a counter-pressure of 7 cm. after 14 days' rest after vulcanization.

All subsequent mixtures were treated in exactly the same way.

1. Problem. In what way does whiting (an inactive filler) influence the overflow?

30% Whiting

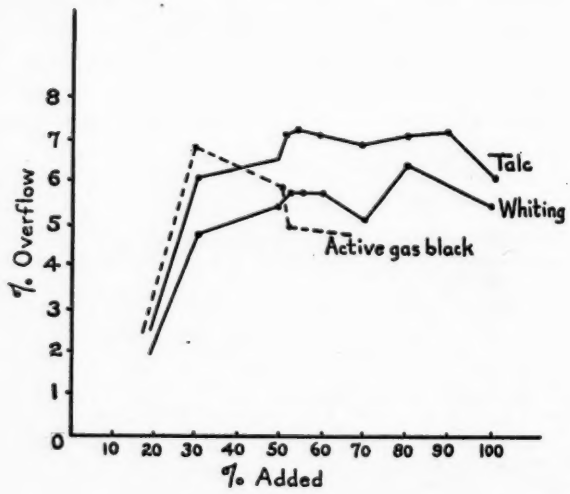
Mixture		Specific Gravity	Volume
Smoked Sheets	10.0 g.	0.89	11.236
Sulfur	0.3	2.07	0.144
Zn oxide	0.5	5.42	0.092
Mercaptobenzothiazole	0.1	1.42	0.070
Whiting (30%)	3.0	2.80	1.071
	13.9		12.613

Experiment No.	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
Whiting	30%	50%	52%	55%	60%	70%	80%	90%	100%
Specific gravity of ball	1.102	1.193	1.20	1.214	1.235	1.275	1.313	1.349	1.383
Wt. of unvulcanized ball in g.	4.62	5.00	5.03	5.09	5.17	5.34	5.5	5.65	5.79
Wt. of ball after vulcanization in g.	4.40	4.73	4.74	4.8	4.87	5.07	5.15	5.26	5.48
Overflow in per cent....	4.75	5.4	5.7	5.69	5.8	5.05	6.3	6.9	5.3
Ball Pressure in cm.....	6.3	6.2	6.1	6.00	6.00	5.7	5.7	5.6	5.5

The next question was whether another inactive filler would give the same per cent of overflow under the same conditions. We selected talc. The investigation may be presented in the simplest and clearest manner in a table:

Overflow With Increasing Proportions of Talc

Determinations	30%	50%	52%	55%	60%	70%	80%	90%	100%
Specific gravity of ball	1.108	1.204	1.213	1.226	1.248	1.29	1.33	1.368	1.405
Wt. of unvulcanized ball in g.	4.64	5.04	5.08	5.14	5.23	5.40	5.57	5.73	5.89
Wt. of ball after vulcanization in g.	4.36	4.71	4.72	4.77	4.86	5.03	5.18	5.32	5.53
Overflow in per cent	6.08	6.54	7.08	7.19	7.07	6.85	7.00	7.15	6.11
Ball pressure in cm.	5.9	5.6	5.0	4.8	4.4	4.2	4.00	3.9	3.6



A similar study on active gas black could be carried out up to the addition of only 60% because mixing became very difficult.

Overflow with Increasing Proportions of Gas Black

Determinations	30%	50%	52%	60%
Specific gravity of ball	1.048	1.104	1.109	1.129
Weight of unvulcanized ball in g.	4.39	4.63	4.65	4.73
Weight of ball after vulcanization in g.	4.09	4.36	4.42	4.50
Overflow in per cent	6.8	5.8	4.9	4.8
Ball Pressure in cm.	6.1	3.4	3.3	2.6

Highly active animal charcoal and finely pulverized silica gel gave no vulcanization with the base mixture studied.

We summarize our important results on overflow in percentages as well as in three curves, from which it is plainly evident that the inactive fillers first cause an increase and then wave-like fluctuations in the overflow, while with active gas black the overflow first increases and then diminishes.

Tabulation of Overflow in Per Cent

	Whiting	*Talc*	*Active gas black*	*Animal Char-coal*	*Silica gel*
Raw rubber, no overflow					
Overflow of 5.02% (base mixture)					
30% Addition	4.75	6.03	6.80		
50% "	5.40	6.50	5.80		
52% "	5.70	7.08	4.90		
55% "	5.69	7.19	—	did	
60% "	5.70	7.07	4.80	not	
70% "	5.05	6.80	—	vulcanize	
80% "	6.30	7.00	—		
90% "	6.90	7.10	—		
100% "	5.30	6.11	—		

The newly discovered fact that vulcanized rubber and vulcanized rubber mixtures have a greater volume than similar unvulcanized mixtures, leads to the surprising conclusion that all calculations of the specific gravity of vulcanizates made since the manufacture of rubber goods are wrong, since they have been based on a false assumption that vulcanized and unvulcanized mixtures had equal volumes. The discovery that the volume of the vulcanizate is always larger than that of the raw rubber mixture and therefore the specific gravity of the vulcanizate is always less than the specific gravity of the raw mixture vitiates all previous factory calculations and also an immense number of theoretical considerations. Only by the use of micromill in the study of the processes of vulcanization is it possible to do accurate mixing. The differences in specific gravity are important; for example, with our base mixture the specific gravity of the raw rubber was 0.944, and of the vulcanizate 0.90.

Summary

1. Raw rubber undergoes no change in volume during vulcanization.

2. Whenever it is vulcanized with sulfur there is an increase in volume.

3. Every inactive filler influences the overflow (increase in volume) in a characteristic way during vulcanization.

4. An increase in the proportion of a given inactive filler influences the overflow curve in a manner characteristic of the filler concerned.

5. Different inactive fillers influence the overflow in various ways.

6. Active fillers influence the overflow curve in a different manner from inactive fillers.

7. An increase in the proportion of a given active filler influences the overflow curve in a manner entirely characteristic of the filler concerned.

8. Different active fillers influence the overflow in quite different ways.

9. The specific gravity of a vulcanizate with sulfur is always less than the specific gravity of the corresponding unvulcanized mixture.

10. All calculations of specific gravity heretofore made in the rubber industry and theories related to them are incorrect because they are based on the false assumption that no increase in volume occurs during vulcanization.

11. Specific gravity determinations of mixtures must be based on overflow determinations.

[Translated from Revue Générale du Caoutchouc, Vol. 7, No. 63, pages 17–22, July, 1930.]

The Dispersion of Gas Black and the Physical Properties of Rubber Mixtures

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Introduction

Many rubber technologists have already shown the importance of the dispersion of pigments in order to obtain the maxima physical properties of rubber mixtures. In a recent publication on the physical properties of gas black Carson and Sebrell[1] state that they do not know of any article based on tests which deals with the relations between the dispersion of gas black and the properties of corresponding mixtures. Wiegand[2] has already shown, in discussing mixtures highly loaded with gas black, that an incomplete dispersion of the pigments is no longer possible if the consistency of rubber falls below a definite value. He states that the lustre on the surface of a sample such as is used to determine tensile strength is a good method of estimating the degree of dispersion. Hauser[3] upholds the idea that certain pigments attain a maximum dispersion during milling. In two preceding communications[4] I studied the distribution of gas black in vulcanized and unvulcanized mixtures. I showed that changes in dispersion occur during milling as well as during vulcanization, and I discussed the theoretical possibility of obtaining the maximum dispersion and reënforcement. On the contrary, I am not concerned in these articles with the actual physical properties of the mixtures examined.

In the present work, I wish to attempt to establish the relations between the dispersion of gas black and certain physical properties of rubber mixtures, whether vulcanized or not. The dispersion was determined by means of the microscope on freshly cut surfaces of mixtures vulcanized and unvulcanized, using a Leitz vertical illuminator and a Zeiss arc lamp as the source of light. Magnified about 300 times, the aggregates of gas black appear like a non-homogeneous black mass, while on the smoother and more homogeneous surface of the rubber the reflection is so increased that the field remains lighted.

The samples selected for microscopic study were cut with very sharp scissors from pieces of rubber. A small piece of the mixture, shaped so as to have two sides as nearly parallel and one as smooth as possible, was cemented to a cover glass with a thick gum or Canada balsam. Rubber prepared in this way must be a little larger than the interior surface of the objective used (16 mm. Zeiss apochromatic). The stage was then raised until the preparation touched the objective, the rubber being parallel to the lower surface of the objective. This position assures as vertical a lighting of the preparations as possible. Microphotographs were made with a Zeiss Homal No. 1 occular, a Zeiss apochromatic objective of 16 mm. and a tube having a length of 190 mm. The images thus obtained were compared with the physical properties of the mixtures.

The method described to determine the degree of dispersion of gas black in rubber is more rapid than that given previously.[5] Moreover, a much larger surface of the substance can be studied in this way, and the preparations require neither vulcanization, freezing, or compression. It is evident that this method is not of

use in the study of the actual dispersion of the particles, but it appears to be excellent for the study of the mastication process.

The dispersions were characterized as follows:

1. Very bad
2. Bad
3. Passable
4. Good
5. Very good
6. Excellent

For this study a base mixture was prepared of the following:

Rubber	100
Gas black	40
Zinc oxide	5
Sulfur	3
Accelerator	0.4
Antioxidant	1
Stearic acid	4
Pine tar	3

A relatively poor dispersion was obtained by the following procedure:

The accelerator, antioxidant, and the plasticizing agent were incorporated in the rubber by mixing, while the gas black, zinc oxide, and sulfur were added in the dry state. According to every indication, an antagonistic reaction took place[6] between the gas black and the zinc oxide. This can be explained on the basis of the chemical activity of the zinc oxide. The latter is able to react with fatty acids naturally present in the rubber, and with stearic acid or other plasticizing agents, causing a diminution of the wetting action necessary to disperse the gas black. Moreover, the particles of black agglomerate during milling as a result of the fusion of the sulfur crystals.

The degree of dispersion of the mixture, poor at first, can be improved by long milling, by friction of the rolls, by cutting, rolling, and refining. The refining

TABLE I

No.	Time of Milling in Minutes and Order of Additions to Mixture	No. of Cuts	No. of Refinings	Degree of Dispersion
1	1000 g. smoked sheet were mixed 15 min. in a laboratory mill (30 × 48 cm.), adding during this time the accelerator, antioxidant, and the plasticizing agent. It was worked on hot rolls to retain the nerve of the rubber (temperature of rolls about 65°). After a new milling of 15 min., gas black, zinc oxide, and sulfur were added in such a way that the entire charge was added during a period of 30 min. From that moment a sample of 200 g. was cut every 3 minutes. The total time of milling was 30 minutes	5	0	(2) Poor, dull surface
2	33 minutes	10	0	(3) Passable. Surface slightly shiny
3	36 minutes	15	0	(3) Passable. Surface slightly shiny
4	39 minutes	20	1	(4) Good. Shiny surface
5	42 minutes	25	2	(5) Very good. Very shiny surface
6	45 minutes	30	3	(5) Very good. Very shiny surface
7	48 minutes	35	5	(4) Good. Shiny surface

was brought about by passing the rubber between two cylinders spaced at a short distance and drawing it into a sort of sheet about 5 mm. thick. During mastication the degree of dispersion was considerably increased, and the mixture acquired a velvety appearance on the fresh surfaces. The aggregates of gas black disappeared slowly, diminishing according to their size. However, after 48 minutes of mastication and refining the degree of dispersion again commenced to become poorer, perhaps because of a flocculation of particles produced by the increased plasticity of the mixture.

Table I shows the method of operation and gives the degree of dispersion obtained.

Microphotographs Nos. 1 and 2 show the surface of the substance in vertical lighting after 30 minutes and 45 minutes of milling, respectively. In Fig. 1 it can be seen that mixtures of black which give a dull surface where freshly cut contain a large number of aggregates, which are the cause of the dull appearance. The disappearance of the aggregates in sample 2 gives the bright lustre and the aggregates are only recognizable here and there. The parallel lines seen on this sample are due to an inequality of the cuts.

This mixture was then left 24 hours in a chamber maintained constant at 21.1 and with a humidity of 65%. Then the coefficient of plasticity of the unvulcanized mixture was determined at 80°.

The changes in the consistency due to increased mixing have been determined by Williams.[7] A modification of the Williams plastometer was used in which, by means of a circular guide, the movement of the upper plate of the press could be kept absolutely parallel. A cylindrical sample of rubber having a volume of 2 cc. was previously heated for 5 minutes at 80°. It was then placed in the press, the plates of which were kept apart by a small steel block. Readings began at the moment when the steel block was raised to allow a weight of 5000 g. to be put on the sample.

The first height H_1 is a constant and is 12.7 mm., corresponding to the spacing of the edges of the steel block selected. The coefficient of flux H_2 is the height in mm. of the sample after 3 minutes of compression. The recovery value is height H_3 in mm. one minute after raising the weight, which permits the sample to regain part of its original dimensions. The consistency of the mixture containing black is expressed by the coefficient of flux H_2, by the recovery value H_3, and by the percentage of permanent deformation

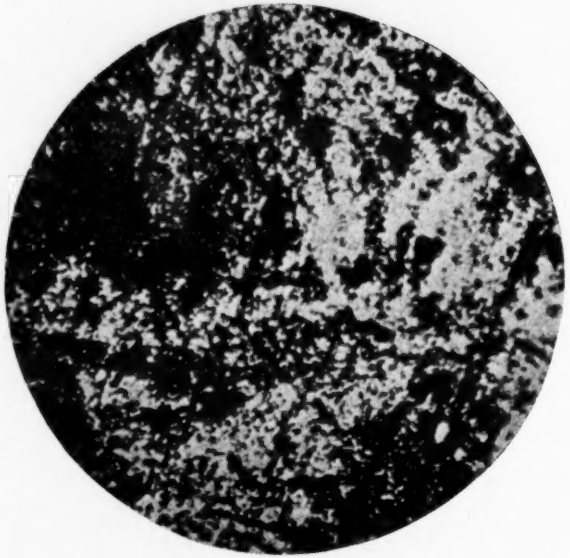
$$\frac{H_1 - H_3}{H_1}$$

Table II again gives the changes in consistency brought about by a progressive mastication and an increas refining.

TABLE II

Time of Milling in Minutes	Coefficient of Flux H_2	Recovery Value H_3	Percentage Permanent Deformation
30	4.53	4.90	61.6
33	4.61	5.10	60
36	4.60	5.07	60.2
39	4.33	4.74	62.5
42	3.88	4.26	66.6
45	3.53	3.87	69.6
48	3.30	3.60	71.7

These values are shown graphically in Diagram 1. From every indication, the plasticity diminished at first, which is perhaps due to the hardening action



1

2

Micrographs

of the black.[8] On progressive mixing, the plasticity increases in proportion to the milling, probably as a result of the grinding of the rubber phase.

CHART I

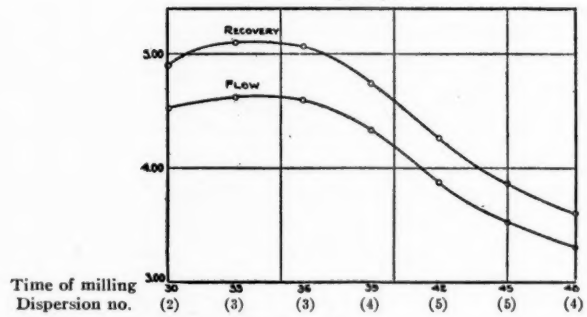


Diagram 1

The influence of milling on the rapidity of the vulcanization of the mixture was then studied. The samples were heated for increasing periods at 141.6° (2.812 atm.) and their tensile strengths determined after being left 24 hours at a constant

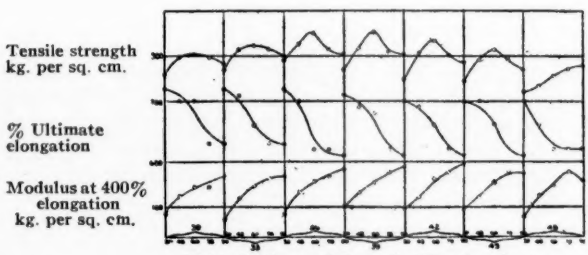

Tensile strength kg. per sq. cm.
% Ultimate elongation
Modulus at 400% elongation kg. per sq. cm.
Vulcanization and time of milling in minutes

Diagram 2

temperature of 21.1°. The tensile strength was determined by means of a Scott machine. The results are given in Table III and are shown graphically in Diagram 2.

It follows from this table that the tensile strength is greatest at a heating of 60 minutes and that the time of milling is unimportant. The mixture does not, however, have a maximum tensile strength with a vulcanization of 90 minutes when mastication has gone on for 40 minutes and 5 refinings have been made. Consequently the physical properties after 48 minutes' mixing cannot be compared with those obtained with other samples of the same series. The curves show, moreover, that continued milling and increased dispersion improve the values for tensile strength and the modulus up to a vulcanization of 39 minutes, beyond which the curves begin to fall again.

TABLE III

Tensile Strength

Time of Milling in Minutes	Time of Heating in Minutes				
	30	45	60	75	90
30	277.71	298.81	302.32	298.80	290.42
33	281.23	309.35	312.16	309.35	300.91
36	295.29	316.38	330.45	309.35	302.32
39	281.23	309.35	331.86	304.43	302.32
42	269.98	302.32	319.89	302.32	292.48
45	267.17	295.29	309.35	295.29	281.23
48	253.11	260.14	274.20	281.23	286.85

Modulus for a Stretch of 400%

Time of Milling in Minutes	Time of Heating in Minutes				
	30	45	60	75	90
30	88.60	112.49	126.55	126.55	140.62
33	84.37	112.49	127.95	137.10	137.10
36	89.27	119.52	133.58	140.62	147.65
39	98.43	118.11	132.15	143.43	154.68
42	98.43	112.49	138.50	144.13	154.68
45	98.43	112.49	130.06	147.65	142.42
48	84.37	112.49	126.55	146.86	135.58

Stretch in %

Time of Milling in Minutes	Time of Heating in Minutes				
	30	45	60	75	90
30	720	700	700	630	630
33	720	710	660	630	630
36	720	700	620	620	610
39	710	690	680	620	610
42	700	690	640	620	610
45	700	700	640	610	610
48	700	660	620	620	620

The ultimate elongation diminishes with the time of milling. On the basis of the accompanying figures, 60 minutes has been selected as the time of heating to study the influence of progressive milling and improvement in the degree of dispersion on the physical properties. The resistance to wear has been determined by the Grasselli machine. The hardness has been determined with the Shore machine. Table IV gives the physical properties of mixtures as a function of both the dispersion and progressive mixing.

TABLE IV

Milling in Minutes	Tensile Strength	Modulus for a Stretch of 400%
30 (2)	302.32	126.55
33 (3)	312.16	127.95
36 (3)	330.45	133.58
39 (4)	331.86	132.15
42 (5)	319.89	138.50
45 (5)	309.35	130.06

Milling in Minutes	% Final Elongation	Resistance to Abrasion	Hardness	Specific Gravity
30	700	254	61	1.12
33	660	216	58	1.12
36	620	209	57	1.12
39	680	199	55	1.12
42	640	208	55	1.12
45	640	240	55	1.12

The tests were repeated many times and the values obtained were always within the limits of error. Diagram 3 shows graphically the relations between the dis-

persion and the physical properties of the mixture. The best results were obtained after mixing for 30 minutes, 20 cuttings, and one refining. The physical properties, like the degree of dispersion, show a marked improvement up to this point. With a

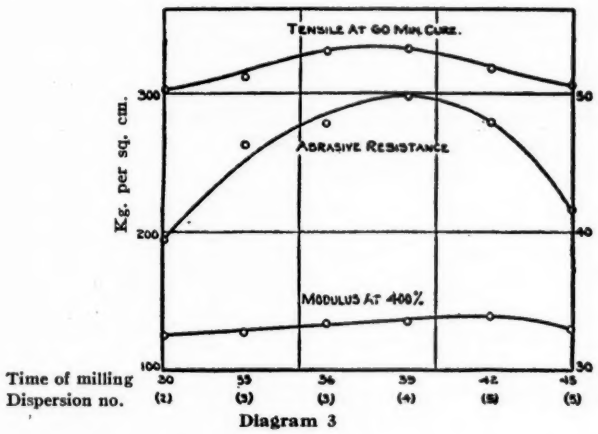


Diagram 3

longer mixing the physical properties diminish and the coefficient of flux of the mixture falls below 4.

Table V gives the results of aging in the Geer oven for 9 days at 70°.

TABLE V

Milling in Minutes	Control	Tensile Strength — Aging in Days — 3	6	9
30	302.32	322.71	302.32	300.91
33	302.16	323.41	305.84	302.32
36	330.45	324.11	316.38	309.35
39	331.86	316.38	302.32	305.83
42	319.09	309.35	299.52	295.29
45	309.35	302.32	300.91	291.78

Milling in Minutes	Control	Modulus for a Stretch of 400% — Aging in Days — 3	6	9
30	126.55	158.19	158.19	168.74
33	127.95	168.74	182.80	182.80
36	133.58	168.74	168.74	187.03
39	132.15	161.71	168.74	187.03
42	138.50	160.30	156.79	175.77
45	130.06	161.71	161.71	175.77

Milling in Minutes	Control	% Ultimate Elongation — Aging in Days — 3	6	9
30	700	610	610	610
33	660	610	570	560
36	620	610	600	600
39	680	590	600	600
42	640	590	610	560
45	640	600	610	530

These results are reproduced graphically in Diagram 4. The final tensile strength for a milling of 30–33 minutes increases in the first 3 days of aging. For all the

other samples a constant diminution can be seen. As is clearly shown in Diagram 5, the particular curve of aging as a function of the time of mixing always remains practically similar to that of the control.

In a previous communication,[9] I expressed the opinion that the physical properties of vulcanized rubber mixtures are governed by the following three factors:

1. The free surface energy of the system, *i. e.*, the surface of contact of the rubber and pigment.
2. The degree of wetting of the pigment by the rubber, *i. e.*, the strength of union between the particles of the pigment and the rubber.
3. The strength of the film of rubber itself.

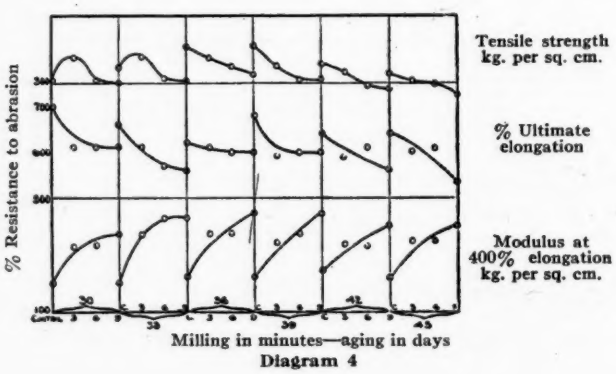

% Resistance to abrasion
Tensile strength kg. per sq. cm.
% Ultimate elongation
Modulus at 400% elongation kg. per sq. cm.
Milling in minutes—aging in days

Diagram 4

The question which must logically be asked is therefore the following: Are the improvements in physical properties obtained really caused by an improvement in the degree of dispersion or rather by an increase in the strength of the rubber film? The generally accepted opinion[10] is that the strength of vulcanized rubber diminishes with increased mastication. Moreover, the fact must be mentioned that rubber mixtures give considerably smaller tensile strength values than a similar mixture prepared under experimental conditions, but using latex that has not been masticated. To study this problem more closely, the combined sulfur of the mixture was determined for a heating of 45 and 60 minutes. The results are given in Table VI.

TABLE VI

Milling in Minutes	Tensile Strength for a Heating of 45 Min.	% Combined Sulfur	Tensile Strength for a Heating of 45 Min.	% Combined Sulfur
30	298.81	1.43	302.32	1.41
33	309.32	1.47	312.16	1.71
36	316.38	1.66	330.45	1.89
39	309.35	1.67	331.86	1.95
42	302.32	1.71	319.89	2.03
45	295.29	1.73	309.35	2.11

From this it is deduced that increasing the time of milling must have caused a decrease in the strength of the rubber phase, which has been proved by an increase in the combined sulfur. Certain physical properties can be influenced to a greater or lesser degree by the combined S. The combined sulfur, however, shows a constant increase, while the physical properties reach a maximum for a time of milling

of 39 minutes, 1.95% of combined sulfur and 60 minutes of vulcanization. This is evident in Diagram 6. Therefore it would appear well founded that the improvement in physical properties obtained in our experiments is due largely to the improvement in the degree of dispersion. It is possible that the adsorption of sulfur by the accelerator and gas black plays a definite role in regulating the physical properties of the mixture, but this subject is to be considered later.

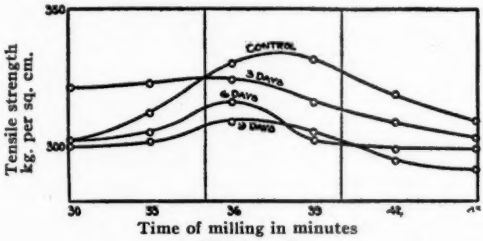


Diagram 5

The observation often made that the physical properties for a given mixture can be obtained both with a good and with a poor dispersion can be explained by the fact that the increase in the strength to be expected from the better dispersion is compensated by a diminution of the strength of the rubber phase during the process of dispersion. The experiments discussed here show that for a given mixture of gas

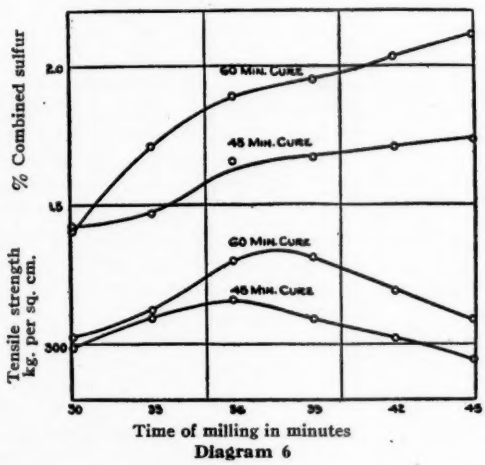


Diagram 6

black there exists a value of optimum dispersion by which the maxima physical properties are obtained.

Résumé

1. A simple qualitative method is suggested for the determination of the dispersion of gas black in heavily loaded mixtures. The method is based on the microscopic study of freshly cut smooth surfaces of mixtures vulcanized or not, using vertical lighting.

2. The improvement in the degree of dispersion obtained by progressive cal-

endering, mixing, rolling, cutting, and refining produces an improvement in the physical properties in so far as the plasticity of the unvulcanized mixture does not drop below a definite figure. In the experiments described this figure corresponds to a coefficient of flux of about 4.

3. There is for a given mixture of gas black a sort of optimum value, which, if maintained under standardized conditions, gives maxima physical properties.

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[1] *Ind. Eng. Chem.*, **21**, 911 (1929).
[2] *Ind. Rubber J.*, **73**, 31 (1927).
[3] "Gow Lectures," page 38, London, **1928**.
[4] *Ind. Eng. Chem.*, **20**, 1071 (1928); **21**, 665 (1929).
[5] *Kautschuk*, **3**, 104, 128 (1927); *Ind. Eng. Chem.*, **13**, 1130 (1921); **17**, 894, 936 (1925).
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Change of Electrical Properties of Rubber and Gutta-Percha during Storage under Water

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Abstract

A number of samples of rubber and gutta-percha were stored under water for about seven years and electrical measurements made on them periodically to determine the effect of aging on the resistivity, dielectric constant, and power factor. The dielectric constant was measured under three different conditions, namely, 60 cycles alternating current, pulsating direct current using 0.6 second charge with 0.1 second discharge, and pulsating direct current using the same time of charge with 1 second discharge. In all cases the dielectric constants increased with time unless failure was approached. A sample was considered to have failed when measurement of its capacitance became impracticable. The changes of the resistivity and power factor varied from sample to sample.

The approach of failure was first indicated by the resistivity. When a curve was plotted with time the sample had been under observation as abscissa and resistance of the samples as ordinates, the curves of the sample which failed showed a break or marked change in direction several months before actual failure occurred. With similar curves for power factor and direct-current dielectric constant, breaks occurred at a later time. The time interval between the break in the resistivity curve and the breaks in the other curves was a function of the rate of decrease of the resistivity. These facts indicate that the failure of a sample is the result of its decrease in resistivity. This decrease in resistivity has been ascribed to the formation of fine holes through the material. This explanation was confirmed by the microscopic examination of microtome sections of the samples which failed. These sections showed fern-like figures projecting into the rubber.

All of the samples that failed were in the form of tubes, with water electrodes both inside and outside the tubes. Some copper salts were inadvertently allowed to form inside the tubes. The catalytic action of these copper salts accelerated the aging, and probably changed its character.

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I. Introduction

The dielectric constant, power factor, and resistivity of a number of samples of rubber and gutta-percha which were stored under water have been observed over a period of about seven years. During this time, measurements have been made

on the average at two months intervals.[1] These measurements showed marked changes in the values of all the specimens.

The changes which have been observed are doubtless the combined effect of oxidation, water absorption, and variations in temperature. As the specimens were always measured at room temperature, the temperature changes produced seasonal changes which can be largely eliminated by drawing smooth curves when the data is plotted with time as one coördinate. However, since water absorption increases with the amount of oxidation,[2] no attempt has been made to separate these two effects.

With some samples, the oxidation has been hastened by catalytic action of copper salts which were inadvertently present. On this account no conclusions can be drawn concerning the normal life of these rubber compounds when stored under water.

II. Description of Specimens

Three classes of specimens were used in this investigation. There were 3 pairs of specimens from submarine cables insulated with rubber, 11 specimens consisting of rubber tubes, and 4 specimens of gutta-percha covered wire.

TABLE I

Specimen Designation	Number of Specimens	Form	Where Obtained	Composition						
				Rubber	Paraffin	Whiting	Zinc Oxide	Sulfur	Talc	Lead Oxide
				Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
A-1	2	Cable	Seattle-Sitka submarine cable	40.5	..	..	5.0	1.9	44.1	8.5
A-2	2	Cable	Seattle-Sitka submarine cable	40.5	..	..	5.0	1.9	44.1	8.5
A-3	2	Cable	Sitka-Valdez submarine cable	..	..	..	..	..	..	..
T-1	4	Tube	Bureau of Standards rubber laboratory	35.8	1.4	..	54.1	2.1	..	6.6
T-2	2	Tube	Bureau of Standards rubber laboratory	40.0	1.4	..	48.9	2.4	..	7.3
T-3	1	Tube	Bureau of Standards rubber laboratory	43.8	1.7	..	45.3	2.5	..	6.7
T-4	1	Tube	Bureau of Standards rubber laboratory	43.5	1.5	..	..	2.2	47.1	5.7
T-5	1	Tube	Bureau of Standards rubber laboratory	56.8	2.2	..	..	3.2	29.1	8.7
T-6	2	Tube	Bureau of Standards rubber laboratory	40.6	1.7	16.6	32.4	2.1	..	6.6
G-4	1	Cable	London	..	..	[a]	..	..	..	..
G-5	1	Cable	London	..	..	[a]	..	..	..	..

[a] Gutta-percha.

The cable specimens with rubber insulation were short lengths of submarine cables which were recovered during repairs to the Alaska cable system. Two pairs

[1] On account of the pressure of other work some of the measurements have been discontinued and others will be made at infrequent intervals. The results to date are presented in the hope that they may be of service to others who may be contemplating similar investigations.

[2] Lowry and Kohman, "The Mechanism of the Absorption of Water by Rubber," *J. Phys. Chem.*, **31**, 54 (1927).

of specimens were taken from the cable which had been laid from Seattle to Sitka, while the third pair probably came from the cable laid from Sitka to Valdez, Alaska. These six specimens are designated by the letter "A." The composition of the specimens taken from the Seattle-Sitka cable as reported by the manufacturing company is given in Table I. The other pair of specimens had a slightly different composition. A complete analysis of the chemical composition of these specimens was not made. However, the ash determination showed that these specimens contained more filler than the other cables. The rubber insulation on these cable specimens was about 2.7 mm. thick, and surrounded a stranded copper wire about 2.5 mm. in diameter. The specimens were about 1500 cm. long.

The tube specimens were made in the rubber laboratory of the National Bureau of Standards, and they are designated by the letter "T." These tubes had a wall thickness of about 1.6 mm., an inside diameter of about 8 mm., and lengths varying from 1200 to 2800 cm. They were quite varied in composition, but were not compounded according to any logical sequence. The exact compositions are given in Table I. In general, the time of vulcanization was such as to give maximum tensile strength, but the time of vulcanization of one set was varied to show the effect of vulcanization on life.

The gutta-percha specimens were taken from samples of gutta-percha cables obtained from an English cable company, and presumably are all alike. They are designated by the letter "G." The diameter of the wire was about 1.6 mm., the thickness of the gutta-percha surrounding it was about 1.7 mm., and the length of each specimen was about 3000 cm.

III. Condition of Test

The outer electrode for each of these specimens was the water in which it was immersed. The inner electrodes for the rubber cable specimens and the gutta-percha specimens were the wires which the insulation covered. An inner electrode for each of the tube specimens was provided by passing a copper wire through the tube and then filling the tube with water. In these cases, then, the water was on both the outside and inside of the specimen.

The specimens were coiled into coils having a diameter of about 25 cm. and placed in galvanized iron containers which were filled with water. The ends of the specimens were made to extend about 15 cm. above the surface of the water in the containers. Guard electrodes were provided by wrapping strips of tinfoil around the specimens about 2 cm. from the ends of the specimens.

The only care given the specimens was that of replacing the water that had evaporated. The mineral content of the water probably increased slowly with time because of the use of ordinary tap water for replacing the water which was lost by evaporation. No attempt was made to regulate the temperature, but records of the temperature at the time that measurements were made were carefully kept. The temperature varied from 13° to 26° C., the average winter temperature being 17° C. and the average summer temperature 25° C.

IV. Electrical Measurements

The capacitance was measured by two different methods, one of which used direct current and one alternating current. Two separate measurements were made using the direct-current method known as the method of mixtures,[3] the difference in the two measurements being that the cycle of voltage application was

[3] H. L. Curtis, "Mica Condensers as Standards of Capacity," *Bur. Standards*, **6**, p. 441 (1910).

different in the two cases. In both cases, the charging time was 0.6 second. During the first 0.5 second of this charging time, the condenser was mechanically connected to the charging battery, while during the last 0.1 second the condenser was insulated. In one case, the discharge time was 0.1 second; in the other case, it was 1.0 second. In this paper the capacitance obtained by these two methods will be called the "tenth-second capacitance" and the "one-second capacitance." The effective dielectric constants computed from these capacitances will be correspondingly designated.

The effective dielectric constant is computed from the capacitance measured at a stated frequency. For other than perfect condensers, the capacitance is a function of the frequency, and thus the effective dielectric constant is a function of the frequency.

The specimens were not made with sufficient exactness to permit an accurate determination of those dimensions which are required for computing the dielectric constant and resistivity of the materials. However, the same values were used in all the computations, so that the indicated changes are relatively correct. These relative changes were more important for this investigation than the absolute values.

The alternating-current capacitance and the power factor were measured at 60 cycles by means of a series inductance bridge.[4] In this paper the capacitance thus obtained will be called the "60-cycle capacitance" and the dielectric constant computed from this capacitance will be called the "60-cycle dielectric constant."

The resistance was measured by means of the direct deflection of a galvanometer.[5]

V. Microtome Sections

Microtome sections were prepared of some of the specimens in order that they might be examined under a compound microscope. As it is impossible to cut thin sections of rubber at ordinary temperature, it was necessary to develop a special technic. The method used was a variation of the method used by Depew and Ruby.[6] It consisted of cooling the specimen to a temperature of approximately $-50°$ C., at which temperature it was sufficiently hard to permit the cutting of thin sections.

The specimen was held in the position for sectioning by freezing it to the top of a block which was clamped to the stage of the microtome. This block acted as a thermal insulator, so that the specimen could be cooled to the desired temperature without cooling the microtome. Firm bond between the specimen and the block was obtained by surrounding the specimen with water and freezing the water by means of a stream of cold air, which also served to cool the specimen.

The stream of air was cooled by means of liquid air. Air obtained from the regular compressed air line of the laboratory was passed through a drying tube to remove moisture and then carried to the bottom of a Dewar flask containing liquid air, so that it bubbled through the liquid, thus cooling to nearly $-180°$ C. Another tube leading from the stopper was directed so that the stream impinged on the specimen. The cooling of the specimen could be regulated by regulating the amount of air which passed through the Dewar flask. The arrangement can readily be understood from the diagram in Figure 1.

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[4] F. W. Grover, "Simultaneous Measurements of the Capacity and Power Factor of Condensers," *Bur. Standards Bull.* **3**, 371 (1907).

[5] H. L. Curtis and A. T. McPherson, *Bur. Standards Tech. Paper*, No. **299**, 679 (1925).

[6] Depew and Ruby, "Some Microsections Cut from Vulcanized Rubber Articles," *J. Ind. Eng. Chem.*, **12**, 1156 (1920).

Since it was not feasible to measure the temperature of the specimen, the correct temperature for cutting the specimen was a matter of judgment. If the specimen was too cold, it became so hard that it was brittle and also injured the microtome knife. If not sufficiently cold, the specimen would give away from the knife and would not cut uniformly. As the cutting was necessarily done by a relatively warm knife, the cutting of the section tended to warm the specimen. Hence, after each cut the specimen was kept under the cold-air stream for several seconds in order to cool it to the necessary temperature for the next cutting.

The sections were permitted to reach room temperature before they were mounted in Canada balsam on a microscope slide after the method used for biological specimens. The most useful specimens had a thickness of from 5 to 10 μ. In examining

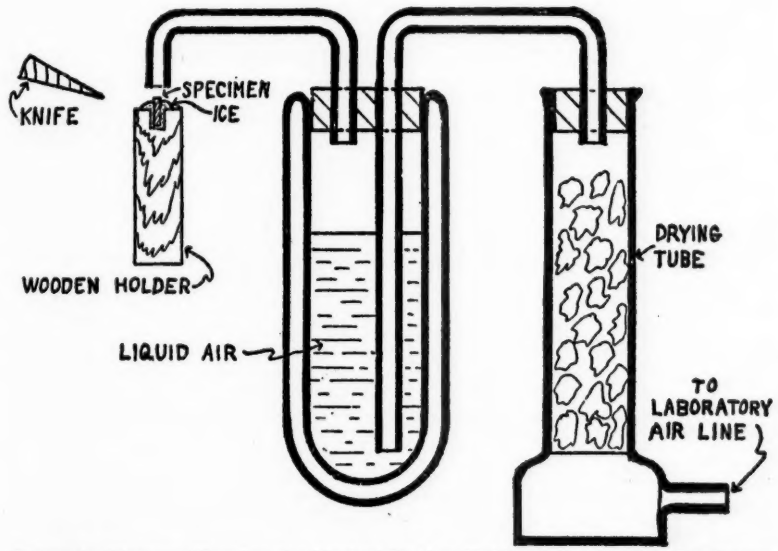

Figure 1—Diagram Showing the Method Used to Hold and Cool Rubber Specimens for Sectioning

The specimen is cemented by ice to the top of a wooden block that is held in the clamp on the stage of a microtome. The ice is kept solid and the specimen cooled to the desired temperature by a stream of air which has been dried and passed through liquid air. The temperature of the specimen, which is regulated by the flow of air through the system, must be low enough so that the specimen will not yield under the pressure of the microtome knife and yet not be so low that the specimen is hard enough to injure the knife.

the specimen a magnification of about 50 diameters gave the most useful information.

VI. Results

On the basis of the results obtained from the electrical measurements, the specimens can be placed in four groups: (1) The rubber cables, (2) the tube specimens which have failed, (3) the tube specimens which have not yet failed, and (4) the gutta-percha covered wires. The complete data on only one specimen of each group are given, attention being called to any significant differences from the other samples of that group. The data are presented in the form of curves, the dielectric constants, power factor, and logarithm of the resistivity being plotted as functions of the time. The specimens which have failed are T-4, T-5, and the

two specimens of T-6. The measurements were continued on these until further capacitance measurements could not be made with the equipment used, at which time the material was considered to have failed. It might appear significant that the samples which failed contained either whiting or talc, but the specimens A-1, A-2, and A-3, not one of which has failed, also contained talc. It is impossible to compare the aging qualities of these two types of specimens as the tube specimens

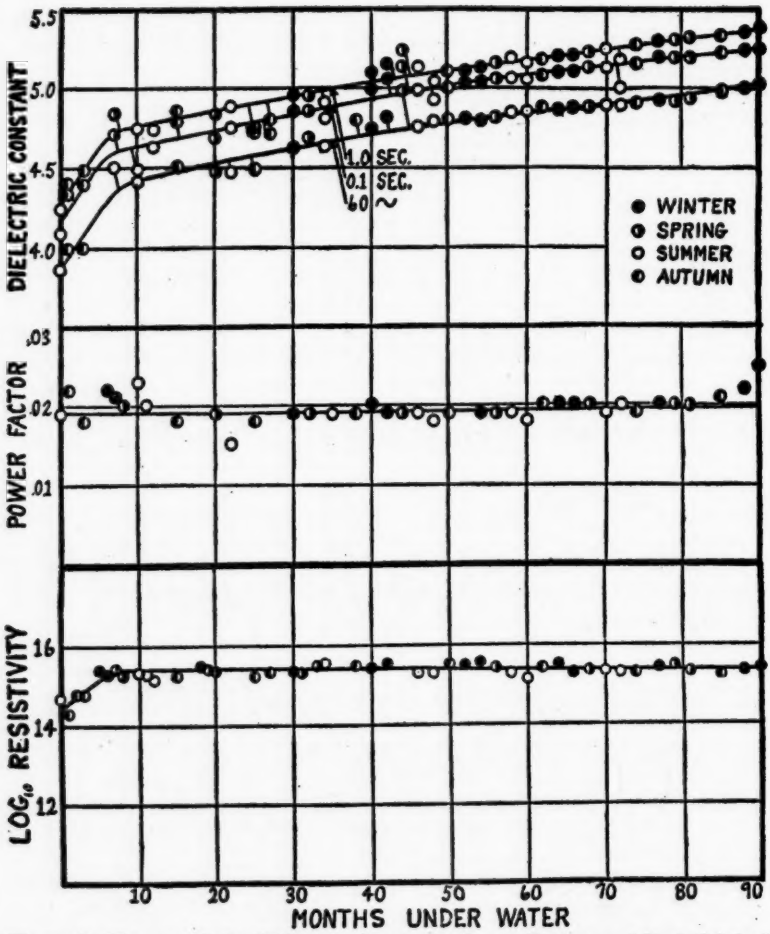

Figure 2—Changes of the Dielectric Constants, Power Factor, and Resistivity of Specimen A-1 with Time Stored under Water

This specimen was selected as typical of the group of submarine cables which did not fail during the 92 months under observation.

were thinner than the cable specimens and their deterioration was accelerated by the presence of copper salts. On the other hand, the cable specimens were in salt water at 4° C. for nearly 20 years before this investigation was started.

The results on A-1, which was selected from the group of rubber cables, are shown in Figure 2. The effective values of the dielectric constant as obtained by the

methods already described are somewhat different at any one time, yet all of them increased at the rate of about 25 per cent in 92 months. The power factor did not show any change with time. The resistivity increased during the first five months, but after that there was no permanent change. However, there were large seasonal variations, as shown by the fact that the black dots (winter observations) are nearly all above the curve, while the open circles (summer observations) are below the curve. This was probably due to the change in temperature at the different seasons.

Of the five additional cables in this group, two gave results which are somewhat different from those of A-1. Instead of remaining constant, the power factors of these increased about 46 per cent, and the resistivities decreased about 75 per cent. However, the change in effective dielectric constant corresponded to that of A-1.

The changes with time of the electrical properties of sample T-1a, which was selected as an example of the tubes that have not yet failed, are shown in Figure 3. All of the three effective dielectric constants increased more than 50 per cent in 85 months, the major part of the increase occurring in the first 30 months. Moreover, with increasing time there is a decided separation of the three curves, the one-second dielectric constant having increased appreciably more than the tenth-second dielectric constant, and this in turn more than the 60-cycle. The power factor showed continuous increase from 0.021 to 0.048, together with very pronounced seasonal variations. The resistivity decreased for the first 30 months, then became nearly stationary. This indicates a closer correlation between resistivity and effective 60-cycle dielectric constant than between resistivity and power factor.

Of the remaining specimens of this group nearly all gave results which differed from those of specimen T-1a in one way or another. In two cases of the same composition, there was no change in the slopes of the curves of the effective dielectric constants, only a steady increase, and in one other case the power factor did not change permanently. The resistivity decreased in all cases, but in three cases there was no pronounced change in slope as was the case of specimen T-1a. There is no evidence that aging in any way depends on the vulcanization. The four specimens of T-1 each had a different vulcanization and there are no marked differences in the changes of the electrical properties of these with time.

The results on specimen T-4, which was one of the group of tube specimens that failed, are shown by the curves in Figure 4. Measurements were continued on this specimen for only 62 months, at which time the deterioration had become so pronounced that no satisfactory measurements could be made. During the first 54 months the effective dielectric constants had increased nearly 100 per cent, the three curves remaining approximately the same distance apart. The resistivity and power factor were constant until failure was approached.

The first indication that the specimen was approaching failure is found in the resistivity curve. At 44 months this curve bends sharply downward making a break in the curve. Ten months later the curves of the effective one-second and tenth-second dielectric constants turn toward the effective 60-cycle dielectric constant, making breaks in these curves. Four months after these breaks there appears to be a second break in the one-second dielectric constant curve when the values which had been decreasing begin to increase. About the time of the first break in the dielectric constant curves the power factor began to increase. However, even to the last measurement, the effective 60-cycle dielectric constant curve showed no break.

The curves for the other three specimens of the group which failed were, in general, similar to the curves of T-4. The resistivity curves for the different

specimens showed breaks at 66, 67, and 76 months. From 3 to 17 months after the breaks in resistivity curves, breaks occurred in the one-second and tenth-second dielectric constant curves, the breaks for the two curves of any one specimen being

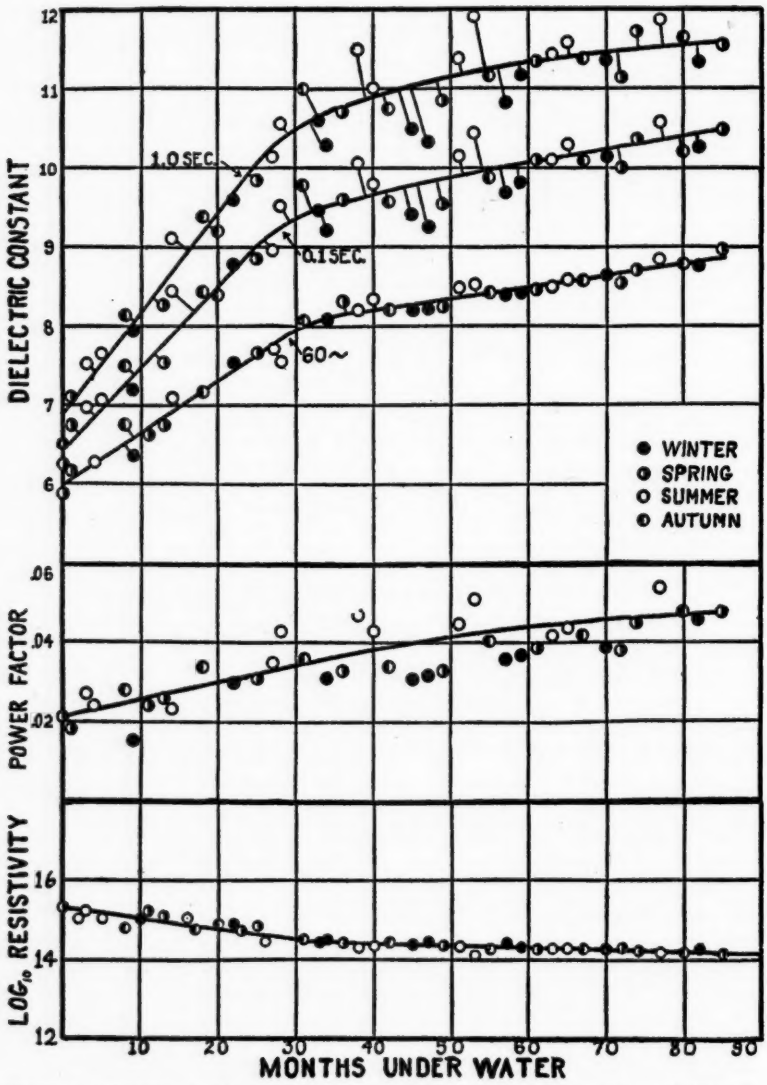

Figure 3—Changes of the Dielectric Constants, Power Factor, and Resistivity of the Specimen T-1a with Time Stored under Water

This specimen was selected as being typical of the group of rubber tubes which did not fail during the 85 months under observation.

simultaneous. At 4 and 6 months, respectively, after the first breaks the one-second curves of two specimens showed a second break, the direction being the

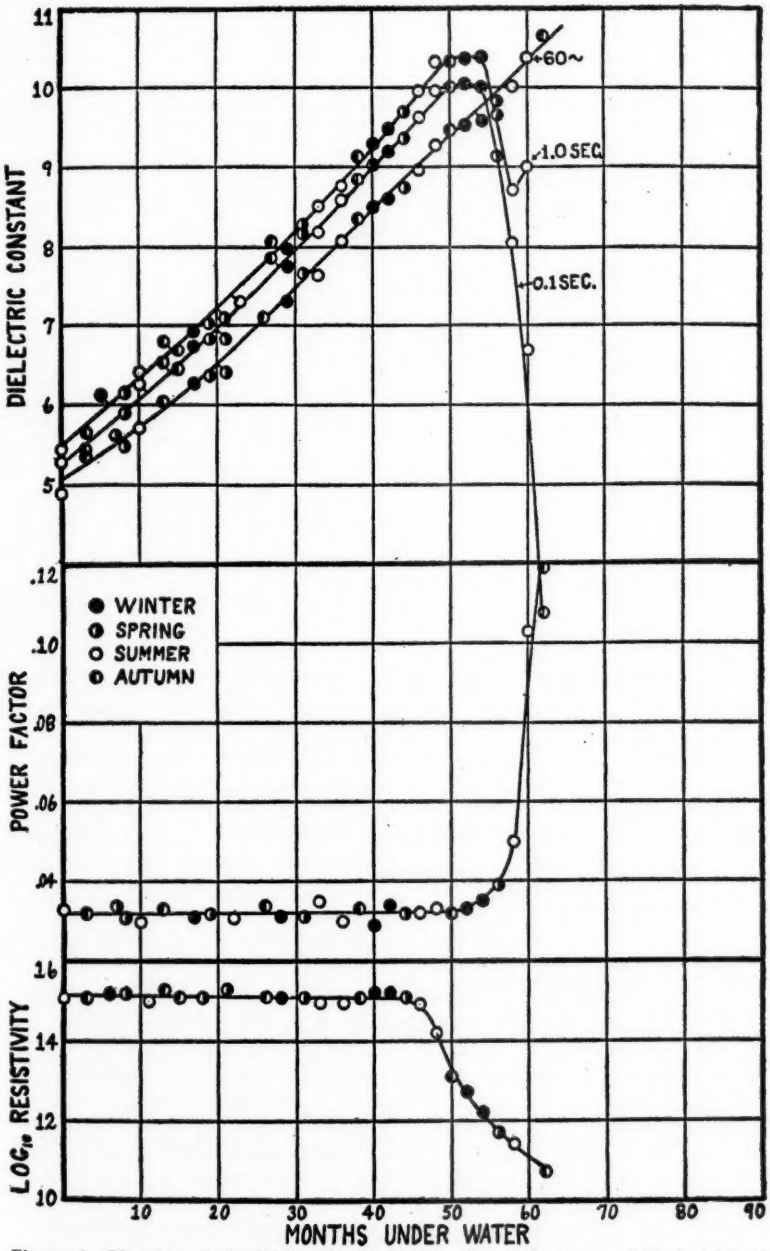

Figure 4—Changes of the Dielectric Constants, Power Factor, and Resistivity of T-4 with Time Stored under Water

This specimen was selected as being typical of the group of rubber tubes which failed.

same as shown in the curve of T-4 (Figure 4), but the magnitude of the change being considerably larger. For every specimen the break in the power-factor curve occurred at the same time as the first break in the dielectric constant curves. For no specimen was there a break in the 60-cycle dielectric constant curve.

In order to determine whether the electrical failure was due to general deterioration or to a local fault, the specimen was tested part by part. It was found that the resistance was low for all parts of the specimen, but that the resistance of the parts near the ends was lower than the rest of the specimens.

This specimen and one of the group of tubes which did not fail were then cut to pieces and carefully examined. It was found that the copper wire which had been run through the length of the specimen was badly corroded and the inner surfaces of the tubes were greenish in color, hard and brittle, indicating that copper salts had promoted the deterioration of the rubber. This was more noticeable near the ends of the tubes where the resistance was lowest. The coating on the inner surface was more pronounced in the specimen that failed than in the one which did not.

The effect of age on the electrical properties of gutta-percha was hard to determine because of the strong tendency for the gutta-percha to crack. In most cases the crack occurred so suddenly that there was no way of observing the effect of approaching failure on the electrical properties. However, in one case the crack developed at a sufficiently slow rate so that these effects could be observed. The changes of the electrical properties of G-4 are shown in Figure 5.

Measurements were made on G-4 for only 71 months, after which time satisfactory measurements were impossible on account of the cracking of the material. During the first 60 months the effective dielectric constants increased about 44 per cent. The separation of the effective dielectric constants was small, but increased with time. The power factor increased from about 0.01 to nearly 0.04 during that time while the resistivity remained nearly constant. The approach of failure was indicated by all the curves except the 60-cycle dielectric constant at about the same time. The changes in resistivity, direct-current dielectric constants, and power factor were very rapid at the end of 60 months. There was a sudden decrease of the effective tenth-second dielectric constant. No measurement of the effective one-second dielectric constant was obtained during the 6-month period between 60 months and 66 months but at the end of this time it was much higher than at the end of 60 months. The decrease of the resistivity was very rapid and large. As in the other cases, the effective 60-cycle dielectric constant continued to increase at about its normal rate through this period.

A summary of the results on all the specimens is given in Table II. Only the 60-cycle dielectric constants are given. The percentage increases with time are about the same for the effective "tenth-second" and "one-second" dielectric constants as for the 60-cycle, though in every case the latter was lower than the tenth-second constant, which in turn was lower than the one-second value. There was a wide variation of the percentage increase of the effective dielectric constant from specimen to specimen, but in every case there was a definite increase. There were even larger differences with regard to change of the power factor, some samples showing no appreciable permanent change with time. The resistivity showed no permanent change with time in two cases, increased in two cases, and decreased in all other cases.

VII. Discussions of Results

The different specimens showed such a wide variation in behavior that very few general conclusions can be drawn. However, the data on every specimen under observation show that the effective 60-cycle dielectric constant increased with time

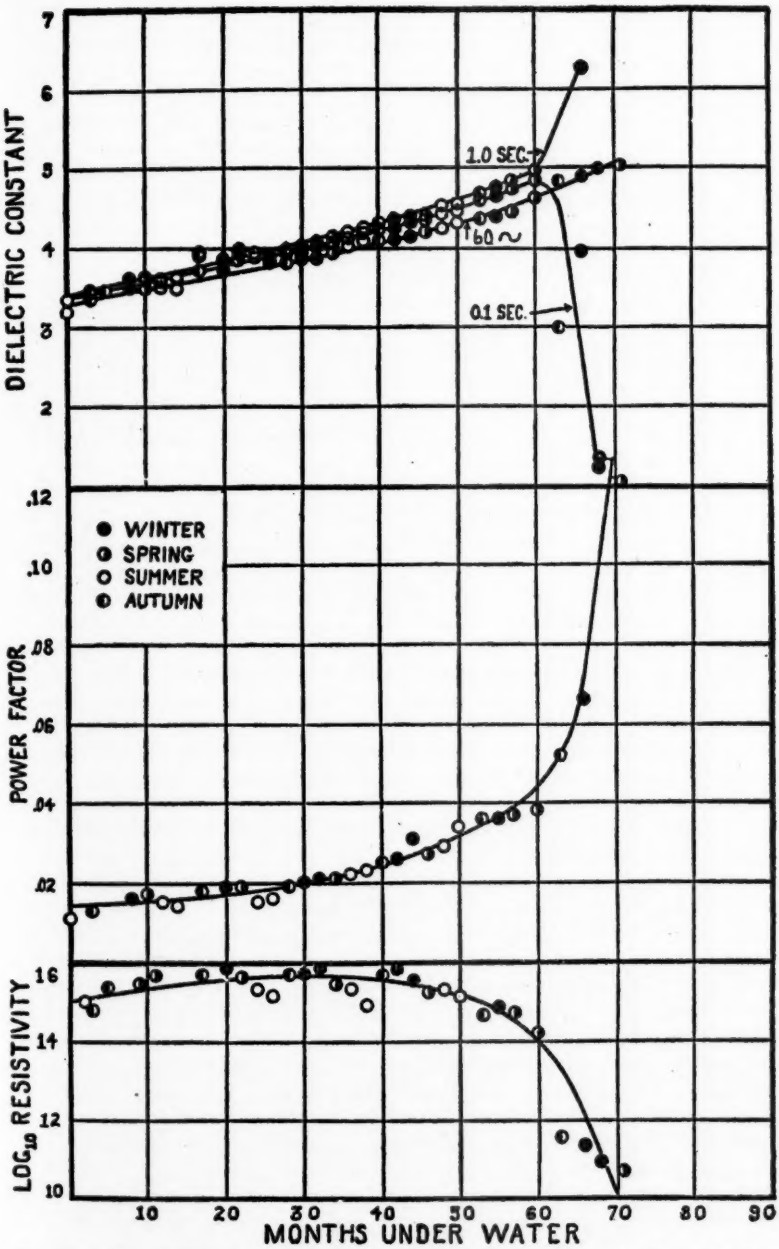

Figure 5—Curves Showing the Changes of the Dielectric Constants, Power Factor, and Resistivity of G-4 with Time Stored under Water

This specimen was one of the gutta-percha specimens, all of which failed.

TABLE II

Type of Specimen	Laboratory Designation of Specimen	Time of Vulcanization at 40-Pound Steam Pressure, Minutes	Time under Observation, Months	Time to Break of—		Effective 60-Cycle Dielectric Constant		Power Factor		Resistivity				
										Value at Break of—				
				Resistivity, Months	Dielectric Constant, Months	Initial Value	Observed Increase, Per cent	Initial Value	Observed Increase, Per cent	Initial Value	Resistivity	Direct Current Dielectric Constant	Final Value	
Submarine cable ...	A-1	.....	92	....	....	4.0	25	0.020	20	5×10^{14}	.....	.....	20	$\times 10^{14}$
	A-1′	.....	92	....	....	4.0	25	0.020	20	5×10^{14}	.....	.....	20	$\times 10^{14}$
	A-2	.....	87	....	....	4.4	7	0.017	9	18×10^{14}	.....	.....	21	$\times 10^{14}$
	A-2′	.....	87	....	....	4.2	7	0.017	9	18×10^{14}	.....	.....	19	$\times 10^{14}$
	A-3	.....	87	....	....	7.0	21	0.026	46	15×10^{14}	.....	.....	5	$\times 10^{14}$
	A-3′	.....	87	....	....	6.9	28	0.026	46	12×10^{14}	.....	.....	3	$\times 10^{14}$
Tube specimens which have not failed	T-1a	15	85	....	....	5.9	53	0.021	130	20×10^{14}	.....	.....	1.5	$\times 10^{14}$
	T-1b	30	85	....	....	6.8	28	0.029	60	16×10^{14}	.....	.....	1.0	$\times 10^{14}$
	T-1c	60	85	....	....	7.0	40	0.041	0	20×10^{14}	.....	.....	1.5	$\times 10^{14}$
	T-1d	120	85	....	....	7.9	50	0.047	9	17×10^{14}	.....	.....	0.05	$\times 10^{14}$
	T-2	15	85	....	....	5.5	70	0.017	100	15×10^{14}	.....	.....	2	$\times 10^{14}$
	T-2′	15	85	....	....	6.1	41	0.020	100	17×10^{14}	.....	.....	2.3	$\times 10^{14}$
	T-3	15	81	....	....	4.7	79	0.010	100	12×10^{14}	.....	.....	3	$\times 10^{14}$
Tube specimens which failed	T-4	30	62	44	54	4.8	120	0.033	4	12×10^{14}	12×10^{14}	0.57×10^{12}	5.5	$\times 10^{10}$
	T-5	30	81	66	69	5.2	100	0.033	12	12×10^{14}	13×10^{14}	0.12×10^{12}	3.7	$\times 10^{10}$
	T-6	40	87	67	84	6.7	70	0.026	0	11×10^{14}	1.9×10^{14}	0.18×10^{12}	18	$\times 10^{10}$
	T-6′	40	87	76	79	5.9	68	0.026	0	10×10^{14}	3×10^{14}	0.11×10^{12}	8.7	$\times 10^{10}$
Gutta-percha	G-4	.....	71	60	60	3.2	56	0.011	250	9×10^{14}	1.6×10^{14}	0.64×10^{12}	5.5	$\times 10^{10}$
	G-5	.....	71	68	....	3.2	52	0.012	250	9×10^{14}	0.1×10^{14}	.....	140	$\times 10^{14}$

as long as measurements were made. This assumes that the dimensions have remained unchanged. Whether this increase was caused by chemical changes or water absorption cannot be determined from the present data.

For those specimens which failed, the approach of failure was first indicated by a marked decrease in resistivity. The observed breaks which occurred in the effective one-second and tenth-second dielectric constant curves were probably caused by the decrease in the resistance of the specimen. The capacitance of the specimen measured with one-tenth second discharge always showed a decrease when the resistance of the specimen fell below 10^{12} ohms, as shown in the next to the last column in Table II. The capacitance measured with one-second discharge always showed a decided change when the resistance decreased to 10^{12} ohms, but this change was sometimes an increase, sometimes a decrease. In most cases, where there was an initial decrease of the one-second capacitance there was later an increase when the resistance had fallen sufficiently low. Apparently this peculiar behavior is brought about by the dielectric absorption of the specimen, but no quantitative relationship has been established. This decrease and later increase is indicated in the curve for the one-second capacitance of Figure 4, though the increase in this case is so small as to have passed unnoticed had it not been for results on other specimens.

The time interval between the breaks in the resistivity and dielectric constant curves is seen to be dependent on the rate of decrease of the resistivity. When the resistivity decreased rapidly this time interval was small. In the case of G-4 this interval was less than that between measurements and, therefore, from the curves it appears that the breaks in both sets of curves came at the same time.

The break in the power-factor curves can likewise be attributed to the decreased resistance of the specimen, and in this case the relation is quantitative. So long as the resistance remains high the power loss, due to conduction through the insulating material, is a negligible part of the total, but after the break in the power-factor curves, the loss due to the decreased resistivity accounts for the sharp increase which occurs in the power factor. A possible exception occurs when the resistivity becomes very low, but under this condition measurements of both resistance and power factor are very inaccurate.

Since all the changes in the observed curves as the specimen approached failure can be explained by the decrease in resistance, it appears that the direct measurement of the resistance is the best method of determining the electrical failure of materials of this kind. This is emphasized by the fact that the break in the resistivity curve occurs several months in advance of the break in any other curve.

The decrease in resistance of those rubber specimens which failed is not caused by a single large hole opening through the insulation, as was shown by the measurements on one of the tube specimens, where the resistance of all parts was low. An explanation which seems to fit the facts can be made by assuming that numerous fine holes, which become filled with water, extend through or nearly through the insulation. The resistivity of water is less than one-trillionth part of that of rubber so that a very few minute holes will explain the decrease in resistance. At the same time the measured dielectric constant would not be appreciably affected by these holes, since the dielectric constant of water is never more than 30 times that of the rubber. Little is known about the power factor of water, but apparently the observed break in the power factor curve is not inconsistent with the above explanation of the cause of failure. While this explanation fits the facts, there may be others which would be equally satisfactory.

The above explanation has been confirmed by observations on microtome sections

of the failed specimens. A characteristic microphotograph of a section is shown in Figure 6. Dark, fern-like figures can be seen extending into the rubber from the surface on the inside of the tube, many for at least one-third of the thickness of the rubber. While none has been observed which reaches entirely through the rubber, this is no reflection on the above theory. The chances of observing one are ex-

Figure 6—Microphotograph of a Section of Specimen T-4

This microphotograph of a section of a tube specimen which failed shows the dark fern-like figures extending into the rubber. These figures are probably caused by the presence of cuprous sulfide.

ceedingly small because few are required to account for the observed resistivities and the portion of the specimen represented by the sections on the slides is minute.

Since this type of deterioration occurred only where copper salts were present

on the surface, it is probable that these salts have combined with the sulfur of the rubber to form cuprous sulfide, which has the dark color observed in the fern-like portions. Since copper salts were present on all samples which were observed until failure occurred, the conclusion concerning the change of electrical properties in the approach of failure may not apply to samples where such salts are not present. However, in a cable submerged in sea water, an insignificantly small penetration of water through an exceedingly small pore might start the formation of copper salts which would rapidly enlarge the hole and cause a failure of the cable.

In some cases there was considerable change of the electrical properties with the season, which probably was due to the change in temperature. This did not show up in the same property in all specimens. In the rubber cables the resistivity varied considerably with the season, while the other properties did not vary so much. In the tube specimens, the resistivity did not change much with the season, while the other properties did change. If the temperature had been controlled, better determination of the effect of time on the electrical properties would have resulted.

The authors wish to acknowledge the assistance of a number of their co-workers at the Bureau of Standards. In particular, the specimens for this investigation were made under the direction of S. Collier, and the early electrical measurements were made by Miss Johanna Busse.

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Phenomena of the Mechanical Deformation of Rubber

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I

It is only during recent years that it has become possible by the use of new technic to detect molecular phenomena produced in the mechanical deformation of substances. As far as metallic substances are concerned, and crystalline substances in particular, the problem has already been solved for the most part. On the other hand, in spite of considerable progress during recent years the study of the deformation of organic substances and of fibers in particular, in which group rubber is included, has not yet been carried on.

The mechanical properties of a crystalline system vary according to whether there is a single crystal or an aggregate of crystals. However, in both cases, the extensibility of the products originates in a displacement of parallel layers, *i. e.*, a sliding of the parts of the crystal along definite crystalline planes, this phenomenon of sliding being irreversible in these substances.

In fact, in these cases the reversible part of the elongation is very weak, and amounts to only a few thousandths of the entire phenomenon. In brief, the phenomena of hardening brought about by deformation (sometimes observable) are due to disturbances of the regular lattice.[1] In particular, the displacement of the atom and the change from its normal position can cause the appearance of irregularities on the surface of sliding.

Contrary to what occurs in crystalline products the deformation of rubber is reversible for the most part, is elastic, and is accompanied by a hardening which is also reversible. X-ray examination, which, as is known, permits the identification of changes in the crystalline structure, shows that in the case of rubber there is an appearance of molecular phenomena entirely different from those observed in the deformation of metals, for example. In the special case of rubber, the sliding surfaces do not play the chief part and there is produced on the contrary, as shown by J. R. Katz,[2] a disarrangement throughout the interior of the substance.

The theories proposed to explain the stretching of rubber can be divided into two groups. According to one of these theories the changes which appear during stretching are supposed to take place among the molecules. According to the other group, these changes take place within the molecules. The first theory assumes therefore that in stretching there is a transformation of the molecules into groups of molecules, the molecules themselves not being changed. In the second group of theories, the essential feature of the changes lies in a transposition of the atom within the molecules.

On the basis of the image of the filiformed primary valence chains, K. H. Meyer,[3] H. Fikentscher, and H. Mark[4] have been able, by making use also of Bragg's sizes of the atom and classical laws on the orientation of valence, to sketch a model of the molecule corresponding to the action of x-rays, which permits a very satisfactory explanation of the mechanical properties of rubber. The model made by these authors has the following characteristics: in the unstretched state the shape of a molecule of rubber is that of a long coiled spiral, in the stretched condition this

spiral becomes extended. Furthermore, Fikentscher and Mark have been able to prove the agreement which exists between this hypothesis of the form of the rubber molecule and the model which was proposed by F. Kirchhof[5] some years ago, as well as with the thermodynamic, elastic, radiographic, and chemical properties of rubber.

Nevertheless, in order to make a quantitative comparison of these hypotheses and of the properties of rubber, it is necessary to increase the experimental data. With this end in view, we undertook a series of experiments, and it is necessary to publish first of all those dealing with an explanation of the special properties of rubber from the point of view of hardening and from the point of view of elasticity in the region of low temperatures.

II

M. Polyanyi and A. Schob[6] proved the very important fact that when unvulcanized rubber is stretched its tensile strength is increased. These authors, working at the temperature of liquid air, then compared the tensile strength of different sam-

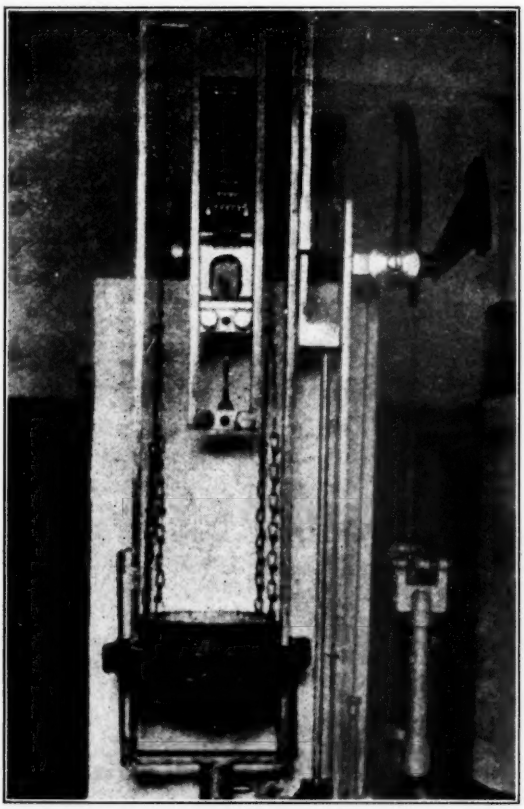

Figure 1—Special Arrangement of the Clamps of the Testing Machine

ples of unstretched rubber with that of rubber previously stretched at room temperature.

L. Hock[7] also observed that rubber which has been stretched and again chilled can be disrupted into fibrous fragments; therefore, if the tensile strength is increased by chilling, the resistance in the direction of stretching is much weaker. Later, E. H. Hauser, P. Rosbaud, and E. Schmid,[8] working under the same conditions as Polanyi and Schob, proved that in this case unvulcanized rubber undergoes the phenomenon of strengthening.

We have carried out these various experiments with raw rubber and with soft rubber vulcanized with a high gas black content, *viz.*, a tire mixture. The breaking tests were made on a Schopper machine whose tension clamps were changed as shown in Figure 1, so as to permit the placing of a Dewar vessel containing liquid nitrogen, which would maintain the sample at a definite temperature. The samples for these experiments were flat strips with enlarged ends.

As the chilling of this device resulted from the exchange of a very considerable amount of heat, the consumption of liquid nitrogen was very large, and reached about 250 cc. for each breaking test. The machine itself was driven by an electric motor. Samples were cut with a steel die out of sheets 1.4 to 2.4 mm. thick. The ends of the test pieces had a breadth of 15 mm. and a height of 5 mm., their middle part having a breadth of 4 mm. and a height of 10 mm. The clamps were placed in the middle of the ends of the test pieces, so that the stretched portion had a total length of 15 mm. In the center of the test piece marks were made 5 mm. apart. The stretch was measured by determining the distance apart of two marks after tension.

The samples were tested in the following ways:

1. Raw rubber from latex (L). From this latex smooth transparent sheets were obtained by evaporation at room temperature and subsequent drying at 30° from ammonia-preserved latex. Tensile strength after test:

For a stretch of 880%: 39.2 kg per sq. cm.

2. Soft rubber (W). This product had the following composition:

Smoked sheet	100
Zinc oxide	5
Sulfur	3
Stearic acid	1
Mercaptobenzothiazole	0.6

Vulcanized at 140° for 50 min. Tensile strength after test:

For a stretch of 827%: 162 kg. per sq. cm.

3. Soft rubber reënforced by gas black (tire compound) (R). Composition:

Smoked sheet	100
Arrow black	40
Stearic acid	4
Zinc oxide	5
Sulfur	3.5
Mercaptobenzothiazole	0.6
Vulcacite D	0.6
Wool grease	2
Aldol-α-naphthylamine	1

Vulcanized at 130°.

The results of these tests are reproduced in Table I and the following chart.

TABLE I

REËNFORCEMENT OF TENSILE STRENGTH OF RUBBER

Previous Stretch in %	Tensile Strength in Kg. per Sq. Cm. at −195° L Raw Rubber from Latex	W Soft Rubber	R Tire Compound
0	360	500	550
100	725	960	1160
200	965	1400	1960
300	1155	1800	2300
400	1390	2330	3280
500	1680	2730	3720
600	2050	3350	..
700	2470	..	..

The figures given above are the average of three and four experiments. The limit of error was about 10%, except for certain values having an error above this figure and which were not used in calculating the average. These results prove that the rubber samples vary in quality at the temperature of liquid nitrogen as well as at room temperature. The curves of the reënforcement of the tensile strength are more nearly vertical and have a more pronounced slope. As a first approximation it may be stated that the resistance of a rubber sample under tension is independent of its previous elongation. For example, a sample stretched fivefold, *i. e.*, with its section reduced to a fifth, broke under the same load as the original sample. Table II gives the similar properties of gutta-percha (commercial Tjipeter).

TABLE II

REËNFORCEMENT OF TENSILE STRENGTH OF GUTTA-PERCHA

Previous Stretch in %	Resistance to Stress in Kg. per Sq. Cm. at −195°
0	350
20	450
30	540
40	640
50	720
100	1000
150	1030
200	1260

Contrary to the opinions of Polanyi and of Schob as well as later work by Hauser, Rosbaud, and Schmid we were not able to prove that the elasticity is greater at the temperature of liquid air for samples which have been previously sketched. In our tests we observed that the elasticity rises to about 10% of the original length and that it then increases in proportion to the previous elongation. We carried out 18 breaking tests on raw rubber previously stretched fivefold so as to be certain of this point. In only three cases did we find an increased value for the elasticity, once 300% and twice 250% of the original length. In the other cases, on the contrary, the elongation was only about 40% of the original length. Since the limits of elongation in the experiments of Polanyi and Schob and in the later tests of Hauser, Rosbaud, and Schmid were very close to the breaking limit, the slight variations in the properties of the substance explain the disappearance of the elasticity.

The fact that, in a general way in our tests, increased elongation was not observed makes it difficult to reproduce the results. In fact, when the elongation is high one no longer measures the resistance of rubber previously stretched at room temperature, but that of rubber previously stretched at room temperature and later

stretched at the temperature of liquid nitrogen, and these two kinds of elongations affect the resistance differently. Independently of this fact, in this case the resistance of the rubber must be related not to the magnitude of the original elongation but to the actual length. Reasoning in this manner, it is found that the values published by Rosbaud and Schmid have a more linear course contrary to that found by these authors, who used the previous elongation as abscissae.

III

We are now going to discuss the molecular mechanism of this reënforcement of rubber as opposed to rupture. The first hypothesis which has been made is here concerned with a micellar orientation of rubber. It is known, in fact, and is a property common to all fibers, that the strength increases with increase in orientation of the fibers. This fact was first proved by R. O. Herzog for artificial silk.[9] In our laboratory we have shown that the tensile strength of films of nitrocellulose increases for an elongation of two to three times this film in the swollen state and changes from 7 to 8 kg. per sq. mm. to 22 to 23 kg. per sq. mm. M. Bergmann and

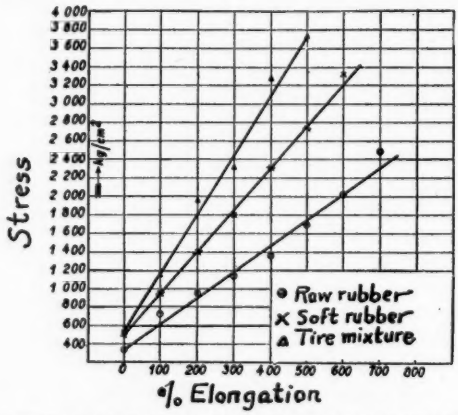

Figure 2—Tensile Strength in Liquid Nitrogen for Different Preliminary Elongations

B. Jacobi[10] have also studied the increase of the tensile strength after drying of gelatine elongated to three times its length in the moist state. Its tensile strength rose from 4.4 to 10 kg. per sq. mm. In the same way, because of the biological interest of this examination we studied, on the advice of Professor K. H. Meyer, the relation existing between the tensile strength of a tendon and its elongation. The tendon of a pig's foot in the natural state gave at a temperature of $-60°$ a tensile strength of 11 kg. per sq. mm. After treatment with warm water and contraction of the tendon by 3.5 times its length the tensile strength at $-60°$ dropped to 3 kg. per sq. mm. If after this treatment the contracted tendon was elongated its original length the tensile strength was 10.6 kg. per sq. mm., *i. e.*, practically the original figure. Almost the same results were obtained when the structure of the tendon was fixed, not by cooling, but by drying. In all the instances we have just examined, x-ray study has shown that elongation causes an orientation of the micelles in the direction of stress.

As far as the mechanism of rupture is concerned, but three[11] explanations can be offered. In the first place, it may be assumed that the molecules regarded individu-

ally are ruptured. Now a simple calculation shows us that the force used in our breaking tests is much too weak to separate the primary valences lying in the same plane. The second hypothesis is that the entangled primary valence chains slide one upon the other and separate. Calculation shows that in this case also the work expended in rupture is much too small to produce this sliding. The third hypothesis, therefore, seems to be the most probable. According to this, whole groups of the primary valence chains, *i. e.*, the micelles, slide upon one another and separate. In this case, the work expended in rupture is still very small compared to the work necessary to bring about sliding, but it may be assumed that there exist groups of defects in the structure which favor the sliding and the separation with the least effort.

This study shows that the reënforcement in the case of these fibers is a result of an entirely different mechanism from that of reënforcement of metals. However, there is one point common to fibers and metals, *i. e.*, the reënforcement in both cases is a geometric phenomenon and not a matter of energy. In the reënforcement of cellulose the question is whether the crystallites or the elongated pseudo-crystallites orient themselves when elongated in the direction of stress which would

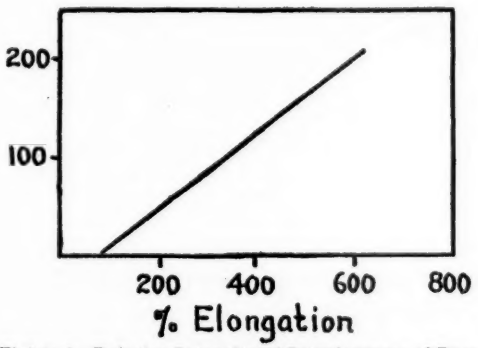

Figure 3—Relative Intensity of Interferences of Raw Rubber Crystals Measured Ionometrically

bring about an increase in the micellar surface perpendicularly to the direction of stress. In the case of rubber and of the tendon, conditions are a little different, since the crystallites are formed only during elongation.

Here it becomes possible to explain the mechanism of reënforcement in a manner particularly clear to rubber technologists. This mechanism would be the following: elongation causes in the rubber an increasing number of crystallized rubber micelles enveloped in an amorphous medium. Elongated rubber is thus formed by a two-phase system containing a very active phase—the rubber crystallites. As raw rubber elongated to a maximum is made up solely of crystalline substance and has a tensile strength ten times greater than that of unstretched rubber, it may be assumed that the tensile strength of the crystallites, whose elongation, orientation, and size do not change during stretching, is ten times greater than the amorphous phase. Consequently the strength of partially stretched rubber should be equal to the strength of the amorphous phase, plus the strength of the crystallites in a given section.[12]

There is, however, an objection to this relatively simple explanation. In effect, it has been proved repeatedly that the intensity of the crystalline interferences

increases linearly with elongation, and only at an elongation of 80% can the first traces of a crystalline structure be detected. At our request, Dr. Hengstenberg studied by means of ionometric measurements the intensity of the interferences of different raw rubbers highly elongated. This method is much more precise than the photometric method which has been used until now. Figure 3 shows that the increase of the crystalline phase for elongations of 0 to 100% is distinctly smaller than the increase for elongations of 100 to 200%. However, the reënforcement is just as great in one type of elongation as in the other.

The problem now is to answer the second question in regard to the behavior of rubber when it passes from the tough state to the brittle. At room temperature rubber can be elongated to many times its length, at the temperature of liquid air, on the contrary, the maximum elongation is less than 10%. It may be asked if the passage from one state to another is gradual or sudden. We studied the properties of raw rubber from the point of view of its tensile strength at temperatures between 20° and −80° and we have been able to show that a somewhat sudden change is

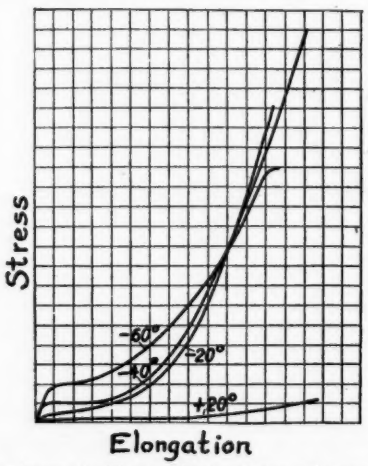

Figure 4—Stress-Strain Curve of Raw Rubber at Different Temperatures

produced at −67°. These tests were carried out on the Schopper machine, using for a temperature bath a mixture of acetone and carbon dioxide.

At room temperature raw rubber samples have an elongation at rupture of about 900% and a breaking load of about 30 kg. per sq. cm. At −20° the elongation is not changed but the breaking load is tenfold. In this case we obtained a tensile strength of 355 kg. per sq. cm., which is a strength that loaded vulcanizates do not ordinarily have. This increase in the tensile strength of raw rubber with lower temperature has already been studied by LeBlanc and Kröger.[13] These authors consider this phenomenon to be a cold vulcanization. The chief difference between this vulcanization and normal vulcanization is that the elongated pieces when cold show a subsequent elastic effect that is extremely large. When the stress is removed the sample returns very slowly to the original condition, and it is only upon reheating that the usual properties of rubber are found.

If the temperature is decreased to lower figures, −40°, then to −60°, no essential change in the properties is observed. The elongation at rupture becomes a little

smaller, about 800%, which is rather remarkable, and the tensile strength also diminishes a little. The division of the stress-strain curve into three sections, which is only slightly noticeable at room temperature, becomes in this case more distinct. Finally, between $-60°$ and $-70°$ there is a very marked change in the stress-strain curve. This critical point quickly appears with high charges, and at a temperature of $-67°$ rubber breaks without very much elongation.[14]

From the work of Hauser, Rosbaud, and Schmid in particular it is known that the stress-strain isotherm depends greatly on the rate of elongation. Our tests have been carried out with an average rate of elongation of about 100% per minute. Unfortunately the Schopper testing machine does not permit a constant rate of elongation because with this machine the elongation cannot be attained independent of the load. It is this mechanical relation between elongation and load in our testing machine that gave the particular shape to the curve in the region of the critical point. In reality, the true significance of the special form of this curve is that the elongation becomes suddenly very rapid for a definite charge. Nevertheless, we were certain in carrying out the following operation that the change sud-

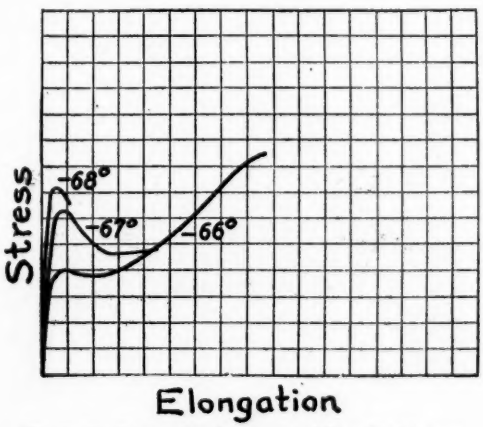

Figure 5—Stress-Strain Curve of Raw Rubber at Different Temperatures

denly observed in the strength of the rubber is actually a property of the substance. In an apparatus which permitted following the elongation of rubber in a low temperature bath with a constant load we studied the properties of different samples of raw rubber subjected to variable stresses in the critical interval of temperature. We loaded the samples at $-66°$ with 10, 20, 60, or 100 kg. per sq. cm. and we observed that the greater the load the more rapid is the elongation. In this case, the time-elongation curve resembles a hyperbola, and the higher the load the more rapidly it rises.

The case is different at $-75°$. For loads of 10 to 60 kg. per sq. cm. we did not once observe for a test lasting fifteen minutes on elongation of 10%. When, on the contrary, we used a load of 70 kg. at the end of two minutes an elongation of about 10% is observed. The rate of elongation increases, therefore, with the time until the sample breaks at an elongation of 400 to 500% after 30 minutes. The curve obtained by plotting the time as abscissa and elongation as ordinate now takes a concave course. In other words, at a sufficiently low temperature there is a load

limit which occurs above the breaking load. Here the resistance to deformation is greater than the resistance of separation. This phenomenon explains this critical point or temperature of brittleness, which, according to the rate that the stress is applied, varies between $-65°$ and $-72°$.

IV

The samples of elongated rubber show very evident signs of brittleness. Above $-66°$, when elongated, the samples become cloudy or milky as at room temperature. If these samples are allowed to return to their normal state, they again become transparent and the cloudiness disappears completely. In the course of these experiments the samples remained entirely homogeneous. If, on the contrary, one works at a lower temperature than the temperature of brittleness, the substance becomes covered with cracks resembling milky white bands, which are still visible for a certain time after heating. It is only by elongation and contraction at room temperature and after a sufficiently long time, sometimes several weeks, that this local turbidity disappears. In most cases the substance presents zones of discontinuity which persist. The photograph represented by Figure 6 shows a sample of raw rubber worked below the temperature of brittleness. If rubber is submitted to a force greater than its limit of extension (in the case of the photograph it was left below this force) and if it is elongated more than 200%, it was proved that most

Figure 6

portions become milky, and under certain conditions, the entire sample becomes milky and remains so, even after heating and suspending the elongation. It is also proved that under these conditions the substance is full of carbon dioxide from the refrigerating mixture. Upon heating, this gas expands in the interior of the rubber and changes its structure, transforming it into a spongy product. This penetration of gas into rubber also takes place during elongation in air or in liquid nitrogen, as has already been shown by Polanyi and Schob, and as we have ourselves observed numerous times.

The explanation of the appearance of these milky bands must be the following. By lowering the temperature the intra-molecular vibration of the spiral molecule becomes slower because the coiled state corresponds to a minimum of potential energy. At the same time, the rate of rotation of translation of the molecule decreases, *i. e.*, the viscosity increases. An increase in the critical point of the curve of deformation in the region of high loads corresponds to the decrease of the intra-molecular vibration. For a sufficiently low temperature the state of equilibrium in the interior of the unstretched molecule is stabilized in the sense that the force required to overcome it becomes greater than the cohesion between the molecules,

and therefore breaking without elongation results. In the region of the temperature of brittleness there can be an extension of the molecule in fixed zones in very special cases, but the sections adjacent to the part of the rubber which undergoes this extension can no longer take part in these changes because of the high viscosity. Under these conditions the substance becomes porous, the pores enlarge, creating a partial vacuum and allowing the gas to enter.

We are now trying in collaboration with Dr. von Susich, to follow radiographically the phenomenon we have just described. We hope, therefore, to make our knowledge of the structure of the rubber molecule more complete.

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[From Recueil des Travaux Chimiques des Pays-Bas, Vol. 48, No. 7–8, pages 681–94, July 15, 1929.]

The Influence of the Amount of the Surplus Liquid on the Swelling Maximum of Rubber Jellies

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It has been frequently observed that the swelling maximum of a jelly is not independent of the ratio of dry jelly to solvent present initially.[1] To explain this behavior Ostwald and Köhler[2] and also Kestenbaum[3] suggest that there are absorbed electrolytes and other impurities present, which influence the swelling

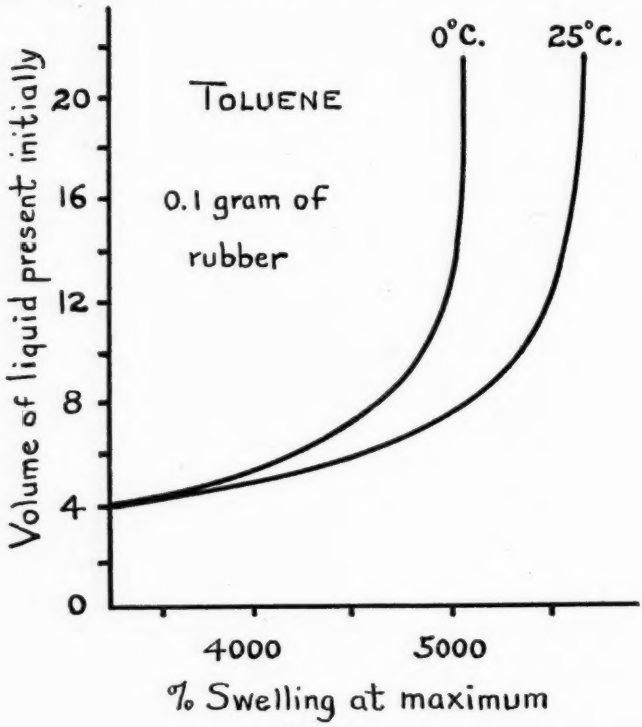

Figure 1

maximum by distributing themselves differently, according to the laws of adsorption, between the jelly and the liquid left if different amounts of liquid are present.

In the case of rubber, on varying the amount of surplus liquid a similar effect has been observed. It could be shown that this is not caused by impurities or other foreign substances present. The influence of the amount of liquid on the swelling maximum was found to be due to the rubber which diffused into the solvent, during the process of swelling, to different extents when different amounts of liquid were present.

For following the effect, pieces of rubber (obtained by drying latex on a porous

plate) weighing exactly 0.1 g. each, were taken and placed with different amounts of solvent in test tubes. The experiments were carried out at 0° and 25° C. The gel was separated from the surplus liquid at intervals and weighed. The time necessary to reach the swelling maximum was noted, and in future experiments one or two weighings only were made.

In the first experiments a highly purified rubber was used. Since no difference in behavior was observed between this and the ordinary dried latex, the latter was used in all subsequent experiments. The following solvents were used: toluene, petroleum ether, and benzene.

The results obtained with toluene for the swelling maximum:

$$\frac{\text{the weight of the swollen gel at maximum}}{\text{the weight of the dry gel (0.1 g.)}} \times 100$$

were plotted against the amounts of liquid initially present, and it is seen that the latter has a marked effect on the swelling maximum. When there is a large surplus of liquid, the swelling maximum becomes independent of the amount present. The effect of low temperature was to lower the swelling maximum, and also to diminish the differences caused by varying the amount of liquid (Figure 1 and Table I).

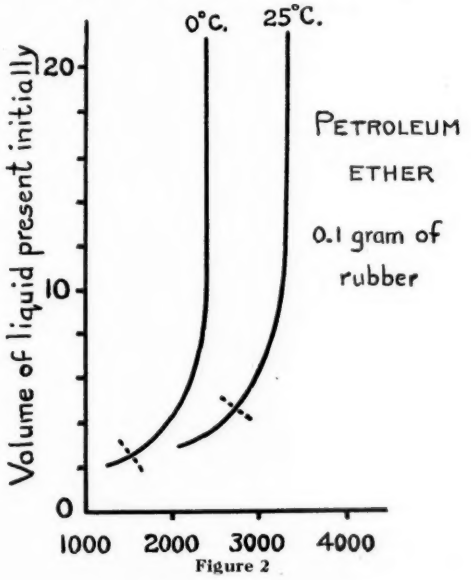

Figure 2

TABLE I

0.1 G. of Rubber in Toluene at 0° C. (90–100 Hours to Reach Maximum) and at 25° C. (60–70 Hours to Reach Maximum)

Volume of Liquid Initially, Cc.	% Swelling at 0° C. (by Wt.)				% Swelling at 25° C.		
4	3300	(no liquid left)			3300	(no liquid left)	
6	4380	4580	..	4200	4480	4590	4270
8	..	4800	4490	4760	5300	5180	5160
10	4720	4820	..	..	..	5230	5560
12	4950	5020	4960	4960	..	5330	5410
15	4850	5200	5400	5190	5490	5670	5650
20	4870	5030	4580?	..	5570	5420	5740
	1st Det.	2nd Det.	3rd Det.	4th Det.	1st Det.	2nd Det.	3rd Det.

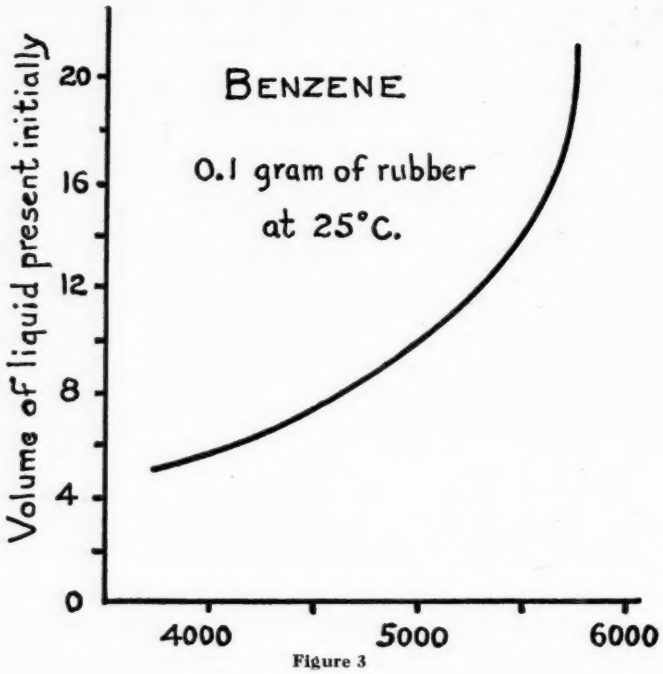

Figure 3

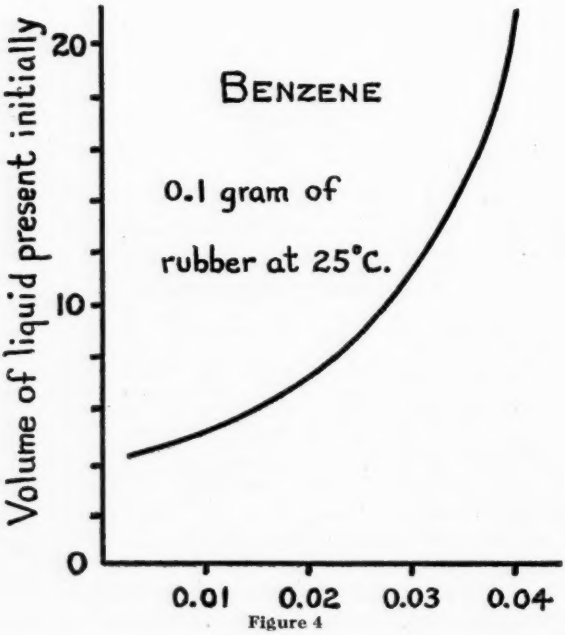

Figure 4

The petroleum ether used boiled at 100°–120° C. This swells rubber in a different manner. The swelling maximum is less and the jellies swollen in this solvent to the same extent as in toluene are more elastic. In this case less of the jelly went into solution. The results are given in Figure 2; it is seen that the effect is very much less marked.

The most probable cause of this behavior as well as that of gelatin is that some of the jelly diffuses into the liquid and this dissolved jelly influences further swelling. This has been shown to be so by following the effect of the concentration of rubber

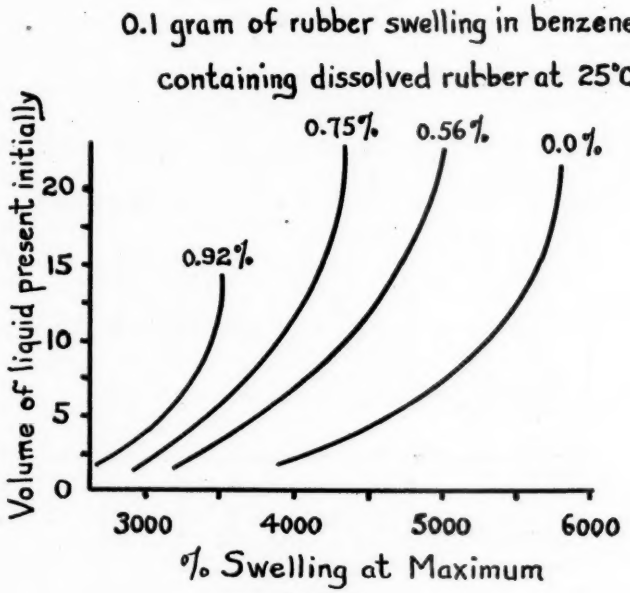

Figure 5

TABLE II

0.1 G. of Rubber in Benzene at 25° C. (60–70 Hours to Reach Maximum)

Vol. of Liquid Initially, Cc.		% Swelling (by Wt.)	Wt. of Dried Gel, G.	Wt. of Liquid Left, G.	Wt. of Rubber in Liquid, G.	Concentration of Rubber in Liquid (Outside), G./100 G.
1st Det.	6	4220	0.087	1.11	0.013	1.17
	8	4830	...	...	...	...
	10	5070	0.075	3.75	0.025	0.67
	15	5690	0.067	7.50	0.033	0.44
	20	5770	0.058	11.79	0.042	0.356
2nd Det.	6	4000	0.088	1.34	0.012	0.90?
	10	4720	0.070	4.10	0.030	0.73
	12	5260	0.073	5.31	0.027	0.51
	15	5650	0.065	7.53	0.035	0.465
	20	6060	0.060	11.50	0.040	0.348
3rd Det.	6	4020	0.082	1.31	0.018	1.37
	8	4520	0.081	2.56	0.019	0.74
	12	5060	0.072	5.51	0.028	0.51
	15	5400	0.065	7.78	0.035	0.45
	20	5650	0.058	11.91	0.042	0.354
4th Det.	6	3900	0.082	1.43	0.018	1.26
	8	4420	0.074	2.65	0.026	0.98

in the surplus liquid. The amounts in solution with different surplus were determined in the case of benzene at 25° C. This was done by drying the gels and weighing them.

It was found that the actual weight of rubber passing into solution was lower the lower the amount of liquid present. The concentration, however, of rubber in the liquid that remained unabsorbed was greater, the lower the amount of liquid present initially. The jelly swelled less in the liquid containing more rubber.

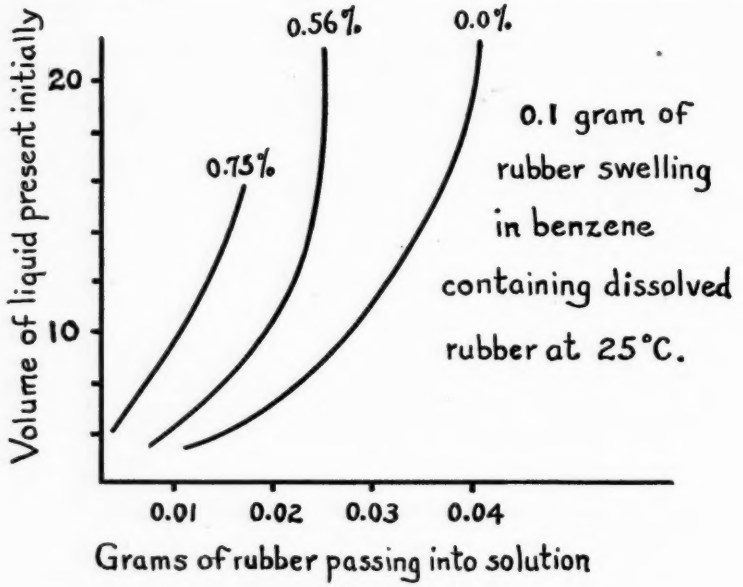

Figure 6

TABLE III

0.1 G. of Rubber in Benzene Containing Dissolved Rubber, at 25° C. 0.56 G. of Rubber per 100 Cc. of Solution

Vol. of Liquid Initially, Cc.	% Swelling (by Wt.)	Wt. of Dried Gel, G.	Wt. of Liquid Left, G.	Wt. of Rubber in Liquid, G.	Concentration or Rubber in Liquid (Outside), G./100 G.
6	3400	0.091	1.84	0.042	2.28
6	3280	0.090	2.05	0.043	2.13
8	3770	0.087	3.31	0.0578	1.75
10	3950	0.079	4.89	0.077	1.58
12	4300	0.077	6.26	0.090	1.43
15	4620	0.076	8.58	0.108	1.26
20	4950	0.075	12.62	0.137	1.08
	0.75 G. of Rubber per 100 Cc. of Solution				
6	2950	0.096	2.40	0.049	2.20
8	3500	0.0935	3.60	0.067	1.86
12	3850	0.086	6.70	0.104	1.55
15	4150	0.083	8.96	0.130	1.45
20	4300	....	13.28	....	..
	0.92 G. of Rubber per 100 Cc. of Solution				
6	2800	} Error in determining weight of dry gel too great			
8	3010				
10	3370				
15	3500				

The curve of the amount of rubber going into solution against the amount of liquid present is given (Figures 3 and 4 and Table II).

The part of the jelly that has diffused into the liquid causes this behavior. Further proof was given by the following experiments. The solvent containing this dissolved rubber in various concentrations was used to swell the rubber. With increasing concentration of rubber a lowering in the swelling maximum as well as a lowering in the amount of jelly dissolving could be observed (Figures 5 and 6 and Table III).

This experiment can hardly be explained in the manner adopted by Ostwald and Köhler[4] in the case of gelatin, because it is improbable that the decomposition products after such careful treatment of the rubber would be present. This could be shown by using a solution of overmasticated rubber, which dissolves easily and entirely in the solvent. The effect of this solution was found to be both qualitatively and quantitatively the same (Figure 7 and Table IV). In this case the amount of liquid has been kept constant and the concentration of rubber in the liquid varied.

The effect of a small percentage of foreign substances in the benzene was to lower the swelling maximum. The results for nitrobenzene are given in Table V.

TABLE IV

0.1 G. of Rubber in 12 Cc. of Benzene Containing Dissolved Rubber at 25° C.

% Rubber Initially, G./100 Cc.	% Swelling (by Wt.)	Wt. of Dried Gel, G.	Wt. of Liquid Left, G.	Wt. of Rubber in Liquid, G.	Concentration of Rubber in Liquid (Outside) G./100 G.
0.00	4720	0.058	5.93	0.042	0.71
0.093	4670	0.060	5.97	0.0512	0.86
0.186	4510	0.064	6.05	0.0583	0.965
0.279	4440	0.069	6.13	0.0645	1.05
0.372	4310	0.072	6.26	0.0735	1.17
0.0465	4130	0.074	6.44	0.0815	1.26
0.50	4100	0.078	6.42	0.0820	1.27
0.625	3760	0.082	6.70	0.095	1.45
0.87	3670	0.089	6.92	0.115	1.66
1.16	3590	0.091	7.00	0.149	2.13

0.1 G. of Rubber in 12 Cc. of Benzene Containing Overmasticated Rubber at 25° C.

0.00	4750	0.062	5.81	0.038	0.655
0.08	4700	0.065	5.87	0.045	0.732
0.16	4600	0.067	5.96	0.053	0.890
0.33	4300	0.070	6.27	0.069	1.10
0.49	4100	0.076	6.48	0.083	1.21
0.66	3890	0.081	6.69	0.097	1.45
0.82	3800	0.087	6.78	0.111	1.64
0.98	3570	0.092	6.84	0.125	1.83

TABLE V

0.1 G. of Rubber in Benzene Containing 1% of Nitrobenzene at 25° C.

Volume of Liquid, Cc.	% Swelling (by Weight) Pure C_6H_6	C_6H_6 with Nitrobenzene
6	4150	3700
9	4850	4000
12	5250	4200
20	5750	4530

Discussion

Ostwald and his pupils have shown that the swelling maximum surplus relation can be calculated on the simple empirical adsorption formula $a = \alpha p^{1/n}$, which he writes $q/m = kv^n$ where q is the weight adsorbed, m the amount of the absorbent, and v the volume of the liquid. The logarithm of this in the case of gelatin was found to be a straight line.[5] The curves for this relation in the case of rubber in toluene at 0° C. and 25° C. in benzene at 25° C. (Figures 1 and 3) are given in Figure 8. For small amounts of liquid the linearity is fulfilled but on further increase of the surplus the curve bends over. In the case of benzene the relations hold better.

If we treat it as an adsorption phenomenon the amount bound on the solid q is

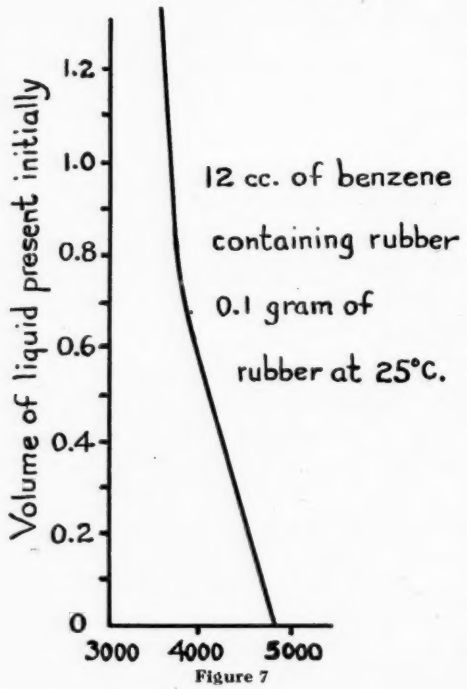

Figure 7

the volume of liquid taken by the jelly. In the case of an adsorption it is hardly possible to imagine that 40 times the weight or volume of the absorbent would be adsorbed. So this similarity cannot lead us to the conclusion that swelling is an adsorption phenomenon. (In the case of parabolic functions it is generally possible to describe the curve with an exponential formula, which has two constants, *e. g.*, Posnjak's exponential formula for swelling pressures.)

The final concentration of the jelly dissolved in the solvent used can be plotted against the swelling maximum (Figure 9 and Table II). Unfortunately the experimental error caused by incomplete separation of the jelly from the liquid was too great to enable definite conclusions to be drawn. This relation seems to be a linear one. If we apply the above-mentioned exponential formula to these results, a linear relation also can be derived (Figure 10): ($q/m = kc^n$; c = concentra-

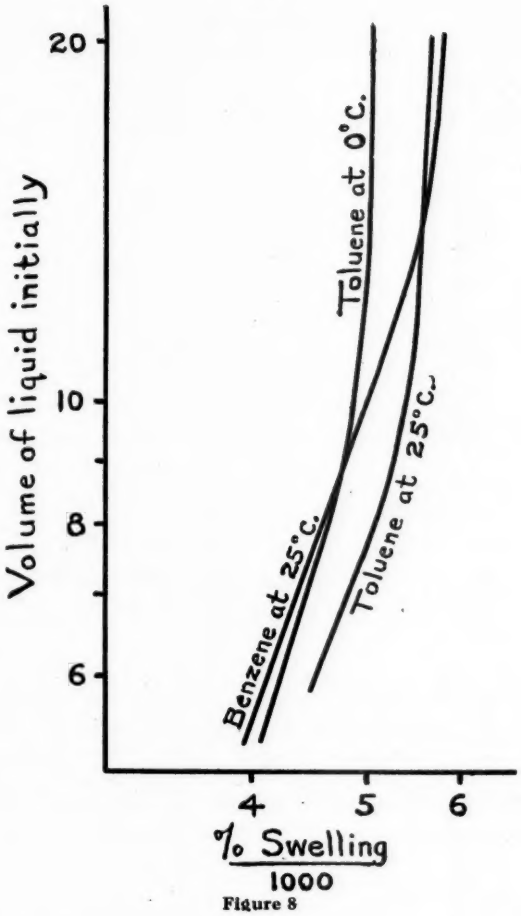

Figure 8

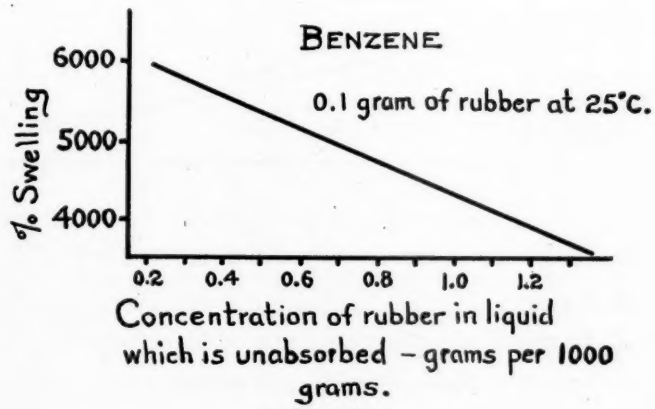

Figure 9

tion of rubber in the liquid in g./1000 g. and q/m = weight of the swollen gel. k = 9.1; n = −0.35). In the cases where rubber was already dissolved a better linear relation was obtained (Figure 11).

It was interesting to follow how far the effect could be made reversible by putting the jelly swollen to its maximum into solutions containing rubber in different concentrations.

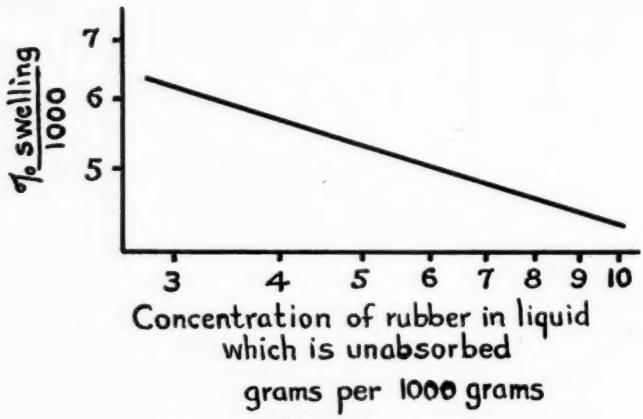

Figure 10

Rubber samples of 0.1 g. swollen to their maximum in 15 cc. of benzene were removed from their solvent and were placed in 9 cc. of benzene containing various amounts of rubber. After 48 hours the samples were weighed. It was found that the swelling gradually decreased and that the loss of weight was greater the greater the concentration of the rubber in the liquid. When the concentration of rubber in the liquid was less than in the first experiment (when the jelly was swollen in pure liquid) the loss of weight was less than for the jelly that had been returned to its

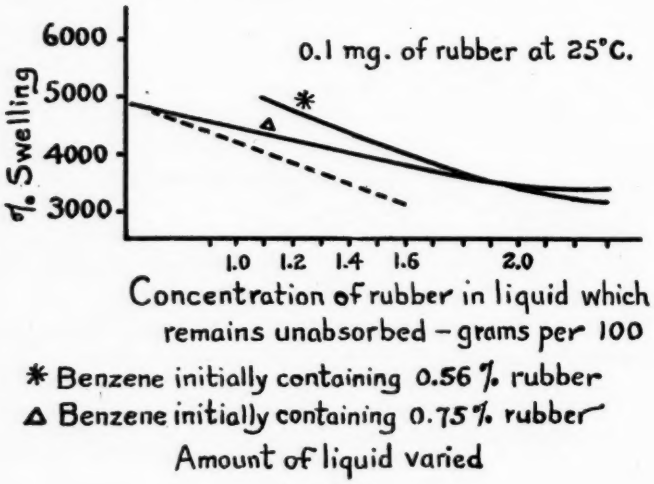

Figure 11

own liquid (marked with* in Table VI). The amount of rubber going into solution after changing the liquid was smaller the higher the concentration of the solution. Both effects were similar to that found when rubber was swollen in liquids which contained different amounts of dissolved rubber. It can be stated that the effect is reversible. Nearly the same final state is observed (by using the same rubber)

TABLE VI

0.1 G. of Rubber Is Swollen in 15 Cc. of Benzene to Maximum at 25° C. The Swollen Gel Is Placed in 9 Cc. of Rubber Soln.

Wt. of Gel in Swollen Condition, G.	Concn. of Solns. into Which Gel Is Put, G./100 Cc.	Wt. of Gel after 48 Hours, G.	Concentration, G.	Wt. of Dried Gel, G.	Approx. Final Concentration of Liquid, G./100 G.
5.26	2.00	3.41	1.85	0.0735	1.87
5.27	2.00	3.55	1.68	0.076	1.87
5.28	1.55	3.74	1.54	0.071	1.49
5.34	1.55	3.80	1.54	0.071	1.49
5.22	1.33	3.80	1.42	0.067	1.29
5.20	1.11	3.70	1.50	0.060	1.08
5.18	1.11	3.92	1.26	0.064	1.10
5.35	0.89	4.11	1.24	0.062	0.93
5.35	0.89	4.30	1.05	0.065	0.94
5.21	0.89	4.08	1.13	0.061	0.94
5.23	0.67	4.35	0.88	0.060	0.78
5.40	0.67	4.56	0.84	0.062	0.78
5.22	0.67	4.28	0.94	0.058	0.77
5.32	0.445	4.75	0.57	0.0565	0.60
*5.32	0.222	4.80	0.52	0.057	0.35
*5.18	0.222	4.60	0.58	0.0525	0.35
*5.40	0.00	4.82	0.58	0.046	0.25
5.26	to its own liquid	4.60	0.66	0.054	0.52
5.25		4.70	0.55	0.056	
5.40		4.68	0.72	0.058	
5.30		4.57	0.73	0.055	

TABLE VII

0.1 G. of Rubber in 15 Cc. of Benzene Containing Dissolved Rubber, at 25° C.

% Rubber Initially, G./100 Cc.	% Swelling (by Wt.)	Wt. of Dried Gel, G.	Wt. of Liquid Left, G.	Wt. of Rubber in Liquid, G.	Concentration of Rubber in Liquid, G./100 G.
2.00	3140	0.100	10.10	0.30	2.97
2.00	3070	0.100	10.18	0.30	2.98
1.60	3360	0.099	9.89	0.24	2.42
1.60	3440	0.097	9.75	0.24	2.46
1.47	3400	0.097	9.80	0.22	2.48
1.33	3770	0.095	9.40	0.204	2.17
1.33	3630	0.095	9.62	0.205	2.13
1.33	3720	0.095	9.50	0.205	2.15
1.06	3700	0.089	9.55	0.171	1.79
1.06	3800	0.093	9.40	0.167	1.78
0.80	4100	0.082	9.15	0.138	1.50
0.80	4100	0.088	9.15	0.132	1.45
0.667	4390	0.082	8.80	0.118	1.34
0.535	4500	0.080	8.70	0.10	1.15
0.535	4640	0.080	8.75	0.10	1.15
0.266	4750	0.073	8.50	0.067	0.79
0.266	4740	0.076	8.50	0.064	0.755
0.133	5150	0.072	8.05	0.048	0.597
0.00	5410	0.069	7.80	0.031	0.398
0.00	5300	0.069	7.90	0.031	0.392
0.00	5150	0.070	8.00	0.030	0.375
0.00	5400	0.069	7.80	0.031	0.398

when the experiments were carried out (1) by swelling the rubber in solvents containing rubber initially; (2) by placing the swollen jelly in rubber solutions (Tables VI and VII).

From the results given above it is obvious that the variations in the swelling maximum are due to the change in the concentration of the rubber in the liquid that is left unabsorbed. The effect has great similarity to an osmotic phenomenon and can be explained qualitatively on this assumption. With the increase of the rubber concentration in the outside liquid the osmotic pressure will be reduced, on account of the decrease of the concentration difference between the outside and inside liquid, and therefore the swelling will be less.

Quantitatively it is difficult to calculate this relation because the pressure of the walls cannot be determined.

But it is only possible to say that the activity of the solvent rapidly diminishes if the jelly is dissolved in it.

Conclusions

It has been shown that the so-called "Bodenkörper" effect is caused in the case of rubber by the rubber itself being present in the outside liquid. Rubber swells to a less extent if the solvent contains some dissolved rubber. This effect is reversible if the swollen jelly is placed into solvent containing rubber. An osmotic assumption may be used to explain this process, but it is not possible to draw definite conclusions as to the exact mechanism.

The authors express their thanks to Prof. F. G. Donnan for valuable help and criticism.

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A Study of Gutta-Percha and Balata by Means of X-Ray Spectra

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The x-ray study of gutta-percha and balata has already been undertaken by G. L. Clark,[1] E. A. Hauser,[2] and his collaborators as well as by E. Ott.[3] Their results are contradictory, however, in many respects. For example, Clark gives different values for the lattice of gutta-percha and for the lattice of balata, while Hauser has observed a difference for the angle of deviation only with stretched samples, and consequently proves that the position of the point interferences of the fiber diagrams is identical for both substances.

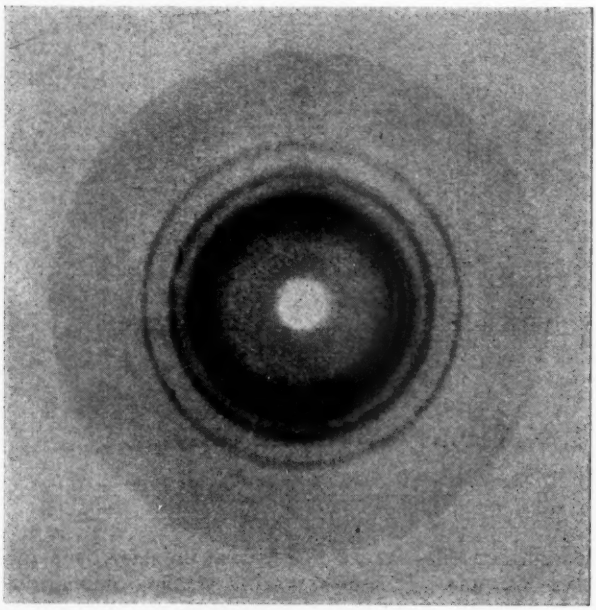

Figure 1—Gutta-α Modification. Copper Radiation. Distance 44.0 ± 0.3 mm.

Moreover Ott's values for gutta-percha vary greatly from those given by Clark. The roentgenographic observations referred to agree only in two respects: 1. Gutta-percha and balata are already crystalline in the unstretched state. 2. The lattice of gutta-percha and of balata is different from that of rubber.

We have studied gutta-percha and balata by means of x-rays with the idea of clearing up the disagreements in previous publications and of determining whether or not there is any difference between gutta-percha and balata.

We exposed to x-rays purified and unpurified[4] samples of gutta-percha and

balata of different origins,[5] in the stretched and unstretched state, at different temperatures (0°–140° C.), as well as after various preparatory treatments, and we established first of all that:

1. Only the hydrocarbon is crystalline. If allowance is made for the amorphous ring of the impurities, which is more or less intense, then it is immaterial for the spectrographic tests whether one exposes purified or unpurified substances to x-rays.

2. As for x-ray spectra, the hydrocarbon of gutta-percha is identical with that of balata. Both have the same lattice, which is different from that of natural rubber, and we can apply to balata without change the x-ray results found for gutta-percha.

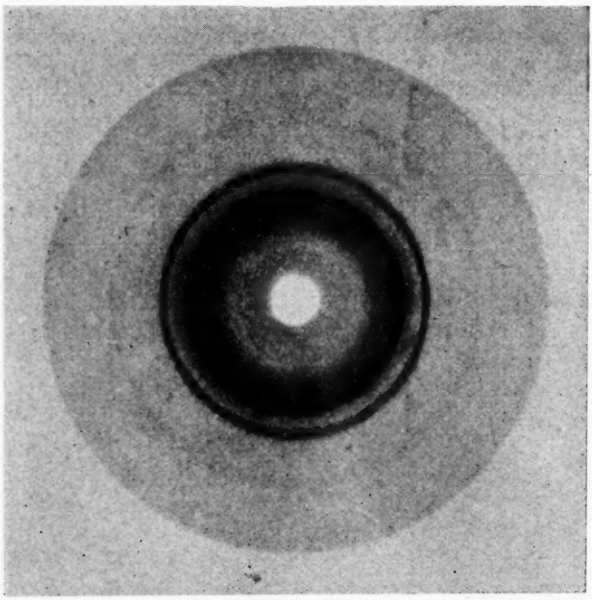

Figure 2—Gutta-β Modification. Copper Radiation. Distance 43.9 ± 0.3 mm.

Unstretched gutta-percha exposed to x-rays at ordinary temperature gives the Debye-Scherrer diagrams. The substance is crystalline but not at all oriented. The diagram in Figure 1 is like that of frozen rubber, published for the first time by Hauser and Rosbaud.[6] The characteristics of this gutta-percha diagram are the first three interferences, corresponding to a spacing of the lattice planes of 4.96, 3.74, and 3.32 Å. U. (Table I). The first of these interferences is very intense, while the other two are a little weaker. If the gutta-percha is heated to about 60° and the sample is then exposed to x-rays after cooling to room temperature, the Debye-Scherrer diagram is still obtained (Figure 2 and Table I), but is unlike that obtained at first. In place of the three interferences there are now only two lines of almost equal intensity (corresponding to a spacing of the lattice planes of 4.73 and 3.89 Å. U.). From these two diagrams it is evident that heating brings about a change in the crystalline lattice. It is a polymorphous transformation similar, for example, to that of rhombic sulfur, which, heated to 95.4° C. is transformed

into a monoclincial modification. In order to distinguish these two forms of gutta-percha and balata we shall designate by gutta-α the form stable at room temperature and by gutta-β that obtained by heating. The transformation of gutta-α into gutta-β was traced as follows: different samples of the same unstretched raw gutta-percha exposed to x-rays at room temperature gave intermediate[7] bands of the Debye-Scherrer diagram. Before exposure to x-rays the samples were heated to 20, 30, 40, 50, 60, 70, 80, 100, 120, and 140° C. for 15 min. and then immersed in water maintained at 0° for 15 min. before the plate was made.

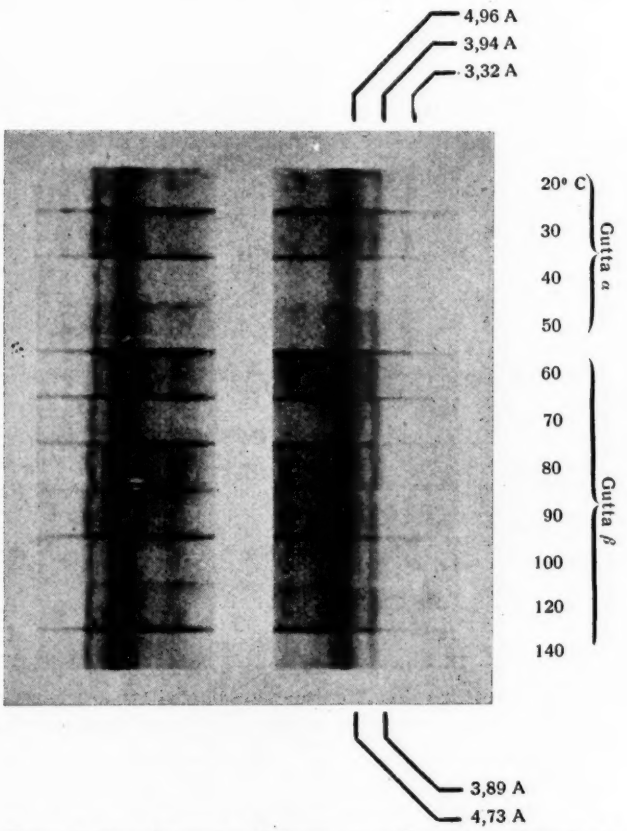

Figure 3—Transformation of Gutta-α into Gutta-β in a Sample of Raw Gutta-Percha. Distance 47 mm.

The diagram shows that the three characteristic interferences of the α-modification disappear on the 5th band (this sample was heated to 60°) and in its place appear the two interferences of the β-modification. It is evident from this negative that the transformation of gutta-α into gutta-β takes place toward 60° for this sample of raw gutta-percha. It should be noted that this transformation point is greatly influenced by impurities present, and we have had some test pieces where the transformation was complete at 40° or not until 80°. Thus, for example, Figure 4 shows the transformation of a purified gutta-percha sample. As in the case of Figure 3,

each piece was heated to 70, 80, 90, and 100°, cooled, and then exposed to x-rays at room temperature. The transformation point for this purified sample is above 80° because the interferences of gutta-β appear only on the third band (sample heated to 90° C.). If samples of gutta-percha heated to increasing temperatures,

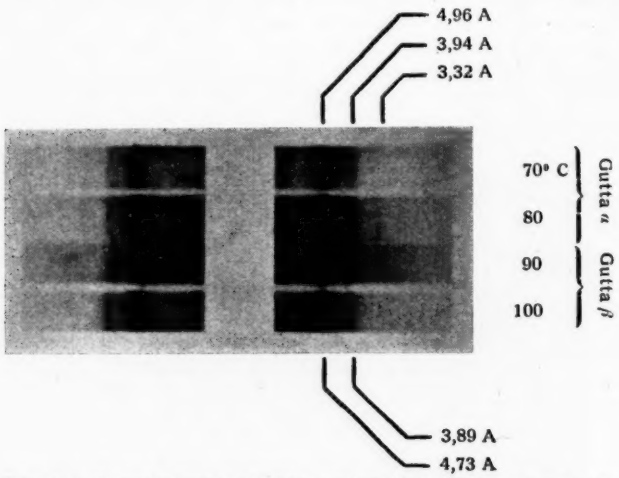

Figure 4—Transformation of Gutta-α into Gutta-β in a Sample of Pure Gutta-Percha. Distance 40 mm.

for example, 20, 30, 40, 50, and 60°, as in the diagram of Figure 5, are exposed to x-rays it is seen that the three interferences of the α-modification disappear completely at 60° (fifth band of Figure 5) and a diagram of an amorphous substance is

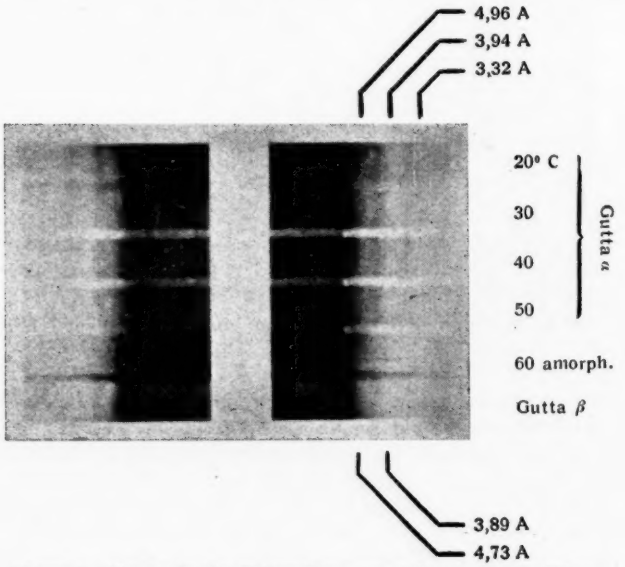

Figure 5—Change in the X-Ray Diagram of Gutta-Percha When the Sample Is Heated and Cooled. Distance 47 mm.

formed. Cooled and exposed to x-rays at room temperature (sixth band of Figure 5) the preparation gives the diagram of the β-modification with its characteristic two lines.

While the transformation of the α-modification into the β-modification takes place easily on heating, it is not easy to pass from the β-modification to the α-form by simple cooling. The heated samples show a marked tendency to remain amorphous for a long time as in the case of glass, and when they at length crystallize the β-modification, which is stable at high temperature, is more often formed. The latter can, however, be transformed into the α-modification if it is dissolved and reprecipitated at a lower temperature than the point of transformation. As this is a discontinuous phenomenon, samples giving a mixed diagram are often obtained. This is the case, for example, if the surface alone of somewhat thick pieces has been transformed into the β-modification.

The temperature at which the interferences disappear and when the diagram becomes amorphous (see band 5 of Figure 5) can, according to the suggestion of J. R. Katz,[8] be called the x-ray fusion point of the unstretched sample. In the case of samples of gutta-percha and balata, however, this point is, like the transformation point, much influenced by impurities[9] present, and is not characteristic of either gutta-percha or balata. Moreover it is not very clear for gutta-percha and balata, while according to measurements by Katz[8] it is quite clear for rubber (*i. e.*, for frozen smoked sheets the x-ray point of fusion lies between 35° and 38°) and corresponds very well to the discontinuous changes of the specific gravity, hardness, and light absorption.[10]

Since gutta-percha and balata can be stretched when warm, fiber diagrams of the β-modification (Figure 6, Table I) can be obtained, which, however, do not approach

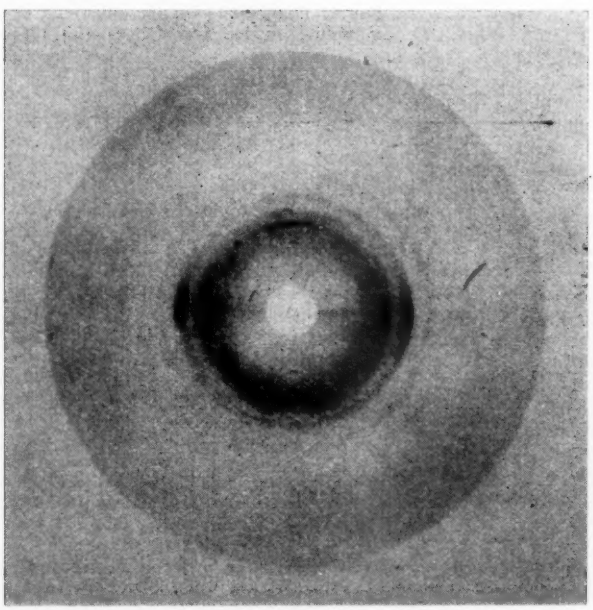

Figure 6—Fiber Diagram of the Gutta-β Modification. Distance 37.9 ± 0.2 mm.

such a handsome fibroid structure as that of stretched rubber. They permit nevertheless the calculation of a fiber period of 4.7 Å. U. According to Clark, the identity period in the direction of the fibers should be 4.6 or 9.3 Å. U., respectively, while Hauser[11] calculates 9.4 Å. U. with his extremely well oriented diagram. Our negatives agree perfectly with an identity period of 9.4 Å. U. This latter could even be deduced from it if the points of interference used by us in calculating the period were not, as we had assumed, on the first and second layer, but on the second and fourth. On Hauser's diagram[11] an intermediate layer is plainly visible (especially for stretched balata), but as we have not observed it with our incompletely oriented samples we must leave unsolved the question of whether the fiber period is 4.7 or 9.4 Å. U.

TABLE I

X-RAY DIAGRAMS

Copper-Potassium Radiation

Gutta-α Modification

Debye-Scherrer diagram. Figure 1

Spacing: 44.0 ± 0.3 mm.

Intensity	2e in mm.	ϑ	sin ϑ	d in Å.U.
Very weak	17.8	3° 27′	0.063	12.2
Medium	25.4	8° 02′	0.140	4.97β
Very strong	28.4	8° 57′	0.155	4.96
Strong	31.0	9° 43′	0.169	4.56
Strong	36.0	11° 16′	0.195	3.94
Strong	49.0	13° 27′	0.232	3.32
Weak	51.6	15° 09′	0.258	2.98
Weak	57.0	16° 20′	0.281	2.74

Gutta-β Modification

Debye-Scherrer Diagram. Figure 2

Spacing: 43.9 ± 0.3 mm.

Intensity	2e in mm.	ϑ	sin ϑ	d in Å.U.
Medium	26.8	8° 18′	0.146	4.75β
Very strong	30.0	9° 20′	0.162	4.73
Medium	32.6	10° 15′	0.178	3.90β
Strong	36.6	11° 28′	0.198	3.89
Very weak	45.2	13° 38′	0.235	3.29
Medium	51.6	15° 8′	0.261	2.95
Weak	56.0	16° 8′	0.277	2.77

Fiber Diagram. Figure 6

Spacing: 37.9 ± 0.2 mm.

	Intensity	2e in mm.	ϑ	sin ϑ	d in Å.U.	cos χ	I in Å.U.
0	Medium	23.6	8° 28′	0.146	4.25		
	Very strong	26.4	9° 20′	0.162	4.73		
	Strong	32.6	11° 28′	0.178	3.89		
	Weak	43.2	15° 8	0.261	2.95		
	Weak	48.2	16° 8	0.277	2.77		
I	Medium	27	9° 55′	0.172	4.48	0.96	4.73
	Weak	43	14° 50′	0.256	3.00	0.68	4.60
II	Weak	53	17° 32′	0.301	4.62	1.0	4.85β
	Medium	60	19° 20′	0.331	4.66	1.0	4.90

Fiber Period 4.7 ± 0.1 Å. U.

The two easily characterized modifications permit the expression of an opinion of the treatments undergone by commercial samples. Especially, if the diagram of gutta-β is obtained by exposure to x-rays, the sample has been heated at a high temperature, but if a diagram of the α-form is obtained, the substance either has not

been heated or has been dissolved after heating and again precipitated at low temperature.

Naturally the presence of the two modifications of gutta-percha and balata must be considered in any study where the transformation point is exceeded, for example, for the viscosimetry of hot and cold solutions.

It is of interest to note that the disagreements in previous publications are due in large measure to the presence of these two modifications, in fact, the authors already cited have been working now with one form, now with the other. Thus Ott has certainly studied the α-modification, Hauser on the contrary the β, and while the values given by Clark for balata approach those of gutta-β, his diagrams of stretched and unstretched balata as well as the values given for gutta-percha correspond to the α-modification.

We sincerely thank K. H. Meyer for having suggested this work to us and also for his encouragement. We also thank Dr. Weil of Hanover in particular for the samples of gutta-percha and balata which he so kindly furnished us.

Résumé

By means of x-ray spectra it has been proved that:

1. The hydrocarbons of gutta-percha and balata are identical, but differ from those of rubber.
2. The hydrocarbon of gutta-percha exists in two polymorphous modifications whose transformation point is about 60° and which depends upon the impurities present.

The modification stable at room temperature (gutta-α) is crystalline even in the unstretched state. The modification stable above 60° C. (gutta-β) is on the contrary amorphous in the unstretched state, like rubber at room temperature. By stretching when hot it becomes crystalline, and oriented, giving a fibrous spectrum by x-rays. For the modification-β, one can calculate from the fiber diagram of the stretched and cooled samples an identity period of 4.7 or 9.4 Å. U., respectively. The x-ray observations of Clark, Hauser, and Ott which are contradictory in certain respects, have been discussed and partly explained by the existence of the two modifications.

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[1] G. L. Clark, *Ind. Eng. Chem.*, **18**, 1131 (1926).

[2] E. A. Hauser, *Kautschuk*, **3**, 228 (1927).

[3] E. Ott, *Naturwissenschaften*, **14**, 320 (1926).

[4] Purification was made as follows: the commercial product was dissolved in chloroform with the addition of 2% of piperidine, the hydrocarbon was precipitated from the filtered solution by the addition of acetone, and finally was extracted with acetone in a Soxhlet in thin sheets, until it was entirely free from resins.

[5] We have not tested latex from gutta-percha and balata, neither have we considered the oxidation of pure hydrocarbons because we have seen no indication that the diagrams are influenced in any way by the oxidation products, which are very difficult to avoid in pure hydrocarbons. It may be assumed that such impurities are amorphous.

[6] E. A. Hauser and P. Rosbaud, *Kautschuk*, **3**, 17 (1927), and *loc. cit.*

[7] The negatives were made with copper radiation in an Ott-Selmayer tube of 5 kv. and 20 milliamperes with 5 minutes' exposure for each operation. These tubes are very well suited to rapid negatives as well as for all qualitative experiments.

[8] J. R. Katz, *Kautschuk*, **5**, 6 (1929).

[9] We have observed samples of very impure gutta-percha which gave, even at room temperature, an amorphous diagram.

[10] A. van Rossem and J. Lotichius, *Kautschuk*, **5**, 2 (1929).

[11] E. A. Hauser, *Ibid.*, **3**, 228 (1927) (see Figures 6 and 7).

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X-RAY INVESTIGATIONS ON RUBBER

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During some earlier x-ray investigations on crêpe rubber, it was observed that the originally translucent sample became more and more milky at the spot where the x-rays passed the material. The sample was the same as described in an earlier paper.[1] This rubber gave a distinct x-ray pattern during the first exposure, but, although the lines did not change their position, they became increasingly sharper with each exposure; simultaneously the opaqueness of the milky spot increased. The increase of sharpness of the originally broad lines represents, of course, increase in particle size; but evidently also the increasing cloudiness of the crêpe rubber shows progressing crystallization.

Another sample of the crêpe rubber was placed in front of the window of the x-ray tube and again slowly the milky spot formed becoming eventually entirely opaque toward transmitted light. The spot obtained was sharply defined by the transmitted x-ray beam and showed no diffuseness at the circumference. After four years of storage, no further changes occurred in the sample. Upon slight warming the milky spot would melt away again.

An increase in the rate of crystallization of gutta-percha, but not of rubber, by means of ultraviolet light was observed by Kirchhof.[2]

Evidently the above sample of rubber behaves similarly under the influence of x-rays as does gutta-percha with ultraviolet light.

[1] E. Ott, *Naturwissenschaften*, **14**, 320 (1926).

[2] Kirchhof, *Kautschuk*, **4**, 254 (1928); *C. A.*, **23**, 1525 (1929).

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Some Aspects of Double Refraction and Structure in Rubber[1]

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Evidence has been presented to show that the micelle in distorted rubber is anisotropic, exhibiting a positive rodlet type of double refraction; that the micelle orients with its long axis in the direction of stretch; and that the micelle orients upon compression as a rodlike structure perpendicular to the direction of compression.

It is proposed that stretch involves an intimate distribution of the soluble viscous hydrocarbon within the gel phase, tending toward an optical homogeneity of the mass and loss of distinction between the two phases.

The double refraction of artificially polymerized isoprene is very similar to that of natural rubber.

Photographs are presented to show the similarity of double refraction in rubber to that of a uniaxial crystal.

EARLY measurements (*1*, *5*) were made to discover a quantitative relationship between double refraction and deformation in rubber, while more recently de Visser (*6*) noted the difficulty of relating calender effect to double refraction, because the anisotropy was found to vanish during the swelling of the material for examination as an optically "mixed body." De Visser believed the sign of the double refraction to be positive, a point of uncertainty in much of the earlier work.

Kroger (*4*) examined the double refraction of a rubber film stretched equally in all directions and concluded that a negative-form double refraction resulted, characteristic of a lamellar structure, in accordance with the Wiener theory (*7*).

Van Geel and Eymers (*3*) examined films of dried latex

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and found the double refraction to be a function of stress similar to the double refraction of liquid crystals as a function of field strength. These authors concluded that an anisotropic alignment of molecules probably exists in stretched rubber.

Zocher and von Fischer (*8*) studied the double refraction of different types of rubber (including frozen rubber) and as an interpretation of the results have proposed the explanation that stretching and racking express a crystallizable substance within the rubber structure. This substance then crystallizes and forms a discontinuous phase.

The present work includes a number of observations of double refraction of rubber under compression as well as under stretch, and an attempt to interpret the behavior in terms of the Wiener theory of micelle double refraction.

Experimental

According to the Wiener theory (*7*, *2*) there is a possibility that crude rubber, consisting of a viscous phase mixed with a gel phase, whose refractive indices do not differ materially, may be considered as a mixed body having two components of the same refractive index. The double refraction, as noted in rubber, would then originate from an optically anisotropic gel micelle. The measurements given in Table I show that both hydrocarbon phases of crude rubber are optically anisotropic under tension. The measurements were made with a Babinet quartz wedge compensator and recorded in wave lengths. Samples were all very nearly 0.5 mμ in thickness and were stretched to 50 per cent elongation. The orange and violet lines of the mercury arc were used as monochromatic illumination.

Table I—Double Refraction Measurements of Rubber

Type of Rubber	λ = 579 mμ	λ = 435 mμ	Change
			Per cent
Diffusion rubber	0.107	0.165	+54
Acetone-extracted whole rubber	0.123	0.214	+74
Benzene-insoluble rubber	0.107	0.258	+140
Polymerized isoprene	0.124	0.237	+91

The data show both of the hydrocarbon phases to be anisotropic upon stretch, at least when examined separately after drying from solution. Difference either in type or size of structure is, however, revealed by the variations noted in double refraction as related to wave length. The double refraction of polymerized isoprene (polymerized by 10 months' heat at 80° C.) is somewhat different from that of rubber, or of the two phases separately.

Stretched Rubber

Since the optical anisotropy of rubber is hardly to be considered that of a mixed body, and since both phases of the hydrocarbon as they exist in rubber are probably capable of exhibiting optical anisotropy when under tension, it is pertinent at this point to consider the mechanism of deformation in rubber as a two-phase action. It is probable that stretch in-

FIG. I. Smoked Sheet

FIG. II. Polymerized Isoprene

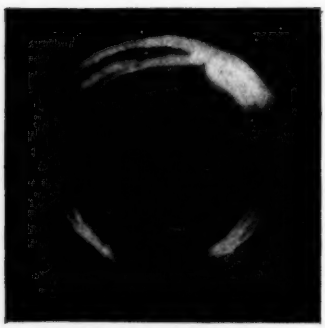

FIG. III. Vulcanized Rubber

FIG. IV. Smoked Sheet with Selenite

Color plates made available through the generosity of the Chemical Foundation, Inc.

Color printing made possible through the coöperation and financial support of the Goodyear Tire and Rubber Company.

volves such a mechanism that the two phases are forced into a physical homogeneity, the soluble viscous phase being forced into a more or less regular orientation position within the interstices of the elongated gel structure. Stretched rubber might therefore be looked upon as approaching an optically uniform mass. The following experiment seems to indicate that this is the case.

If a ribbon of slightly milled smoked sheet is stretched while submerged in benzene or ether, a swelling and disintegration of the rubber takes place within a few seconds, thus making it probable that the gel network upon stretch opens so as to imbibe any available liquid, provided the liquid is miscible with hydrocarbons. Stretching first and then submerging in the solvent produces, but greatly retards, the same effect. Stretching in the absence of a solvent might thus involve a redistribution of soluble hydrocarbon phase within the distended gel network, an action which might easily account for the Joule effect and offer a basis for the explanation of the racking effect. At any rate, the double refraction of stretched rubber is probably that of an intimate mixture of two components having very nearly the same refractive index and both having optical anisotropy under the orienting forces of stretch, and will be considered as such in the following discussion, no attempt being made to distinguish between the two hydrocarbon phases so far as optical anisotropy is concerned.

According to the Wiener theory (7) the character of the oriented micelle may be ascertained by an analysis of the double refraction of the material in the presence of imbibed liquids of different refractive indices. If double refraction persists in the presence of a liquid having the same refractive index as the dispersed phase, the micelle is itself anisotropic and non-spherical. Further, by noting the sign of the double refraction when the index of the imbibed liquid varies from that of the material under examination, it is possible to learn something of the shape and orientation of the component micelles.

If a thin ribbon of rubber is stretched between crossed nicols in a direction 45 degrees to the plane of polarization, and its double refraction observed in conjunction with a selenite plate, it will be noted that the direction of vibration of the extraordinary ray is colinear with the direction of stretch and is the slower vibration. The sign of the double refraction is therefore positive.

The index of refraction of both natural and synthetic rubber (polymerized isoprene) is 1.5350 as measured on the Abbé refractometer, with precautions to insure optical contact between the specimen and glass prisms. A sample of fairly pure chlorobenzene was found to have the same index of refraction at 25° C. as measured on the Abbé. This liquid, therefore, when mixed with rubber hydrocarbon, should destroy the "form double refraction" and leave no optical anisotropy unless the micelles are themselves active. When a thin

ribbon of rubber was allowed to soak in chlorobenzene for several hours, the ribbon was completely permeated yet practically no swelling at all could be noticed. When the rubber with its imbibed liquid thus prepared was gently stretched between crossed nicols, double refraction was found to be intense and positive in sign. The experiment was repeated with the following liquids:

Liquid	Refractive Index (n_D)
Acetone	1.359
Amyl alcohol	1.408
Aniline	1.586
Iodobenzene	1.627

The mixed bodies so obtained were all found to exhibit positive double refraction. These liquids have refractive indices ranging both above and below that of rubber. Thus, positive form double refraction, positive residual double refraction, and optically positive micelles appear to exist in stretched rubber. On the basis of the Wiener theory, this indicates that upon stretch the rubber mass is composed of rodlike micelles oriented with their long axes in the direction of stretch.

Compressed Rubber

If a small right circular cylinder of rubber about 1 mm. in thickness and 2 mm. in diameter is placed between two microscope slides and viewed between crossed nicols in convergent light, no double refraction appears until the sample is gently compressed. If the force of compression is applied at right angles to the observation direction, the double refraction is uniform across the field and fairly intense; if the compression is applied in a direction colinear with that of observation, the dark cross appears which is characteristic of uniaxial crystal sections cut perpendicular to the optic axis and viewed in convergent polarized light. More intense compression causes more intense deformation and thus greater double refraction until at length concentric color circles (using white light) appear.

Similar results may be obtained with polymerized isoprene and vulcanized rubber, photographic records of which are shown in Figures I, II, and III. The symmetry of the figures evidently depends upon the approach of the dimensions of the specimen to geometric perfection and the uniformity of compressional force over the entire field. Many samples were thus prepared and examined with a mica quarter-wave plate in order to determine the sign of the double refraction by displacement of color rings. It was impossible, however, to arrive at a decision about the sign. The cause of failure is of interest and is apparent from the behavior of the compressed sample viewed through a selenite plate; the field appears as is shown in Figure IV. The selenite plate used was of such a thickness that it appeared uniformly first order red between crossed nicols; a substance having a small positive double

refraction arranged with its fast vibration direction parallel to that of the plate raised the color to yellow; in the direction at right angles the color shift was to green. In Figure IV it will be noted that the cross is still red, indicating no double refraction in the plane of polarization and in that at right angles to it. The adjacent quadrants are colored yellow and green, indicating a radial or tangential arrangement symmetrical about an axis passing through the center of the figure and parallel to the direction of compression. The color of the quadrants is dependent upon the relative positions of the sample with respect to the position of fast vibration direction of the selenite, being always yellow in those opposite quadrants bisected by a diameter colinear with the fast vibration direction of the selenite. It was found later that this color also appeared when rubber ribbons were stretched in the same direction over the selenite.

Repetition of the above experiment in compression but using lubricated glass surfaces in contact with the rubber gave entirely different results. Here the double refraction under extreme compression was always feeble and gave no cross. The brilliant color effects noted above must therefore be caused by anisotropy due to frictional shearing in a direction oblique to the direction of compression. Hence the forces of distortion in the unlubricated case giving rise to the color pattern are really those of stretch and the result would be identical with that of stretching in a given direction. Thus the pattern shown in the photograph is really that of radially oriented rodlets.

Acknowledgment

The author wishes to express his thanks to C. H. Barnstorff, Goodyear photographer, for the natural color photographs.

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Water Absorption of Rubber Compounds[1]

H. A. Winkelmann and E. G. Croakman

PHILADELPHIA RUBBER WORKS COMPANY, AKRON, OHIO

The water absorption of a vulcanized rubber compound is of considerable importance in evaluating a rubber compound. In this study it has been shown that fillers such as whiting, barytes, clays, zinc oxide, thermatomic carbon, and carbon black have different effects on the water absorption. Thermatomic carbon gives the lowest water absorption. Volume loading apparently has very little effect. Water absorption of vulcanized rubber decreases with increased time of cure, reaching a minimum at the optimum cure, after which it increases again.

Rubber under stretch absorbs water faster than at rest. A tread compound which has been immersed in water and subsequently dried gives higher physical tests than the original compound. The presence of metallic acetates in a vulcanized rubber compound causes an increase in the water absorption. A hard-rubber compound absorbs water in much the same manner as a soft-rubber compound, but decreases rapidly as the optimum cure is reached. Reclaimed rubbers vary considerably in water absorption, those having the greatest amount of residual alkali present giving the highest water absorption. Shoe reclaim has the lowest water absorption.

RUBBER products which are exposed to moisture and water under varying conditions should have as low water absorption as possible. A study of the variables which might have an effect on the water absorption, such as the effect of various compounding ingredients, volume loading, time of cure, the effect of tension, and the effect of

[1] Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

the presence of salts in the rubber compound, has been made. The results indicate certain facts which may be of value in the preparation of water-resisting compounds. The water absorption was determined on compounds containing whiting, barytes, clay, zinc oxide, thermatomic carbon, and carbon black, respectively. The effect of volume loading and of time of cure was determined for each individual ingredient. Samples representing a range of cure for each compound were immersed in water at room temperature and the percentage increase was recorded at intervals over a period of 30 days. The effect of the presence of various metallic acetates in vulcanized rubber on water absorption is shown. In the tread compound the effect of water absorption on the physical properties was determined. The influence of time of vulcanization on the water absorption of a tread compound is shown. The importance of the choice of the proper reclaim is shown in the comparison of the rate of water absorption of various reclaimed rubbers.

Effect of Fillers

The following pure-gum compound was used as a control in making the water-absorption studies:

Smoked sheets	93
Zinc oxide	3
Sulfur	5
Diphenylguanidine	0.75

To this compound 5, 10, and 15 volumes of whiting, barytes, clay, zinc oxide, thermatomic carbon, and carbon black were added. Each compound was cured 20, 40, 60, 80, 100, and 120 minutes at 141.7° C. The test pieces 2 × 2 × 0.1 inch (5 × 5 × 0.25 cm.) were cut from the cured slabs and immersed in water at room temperature (28° C.).

The percentage increase in weight of the test pieces was determined at various intervals for 30 days. The test was then discontinued because it was felt that this was sufficiently long enough to show the trend of water absorption.

There is practically no effect of increased volume loading of any given pigment on water absorption. This is illustrated by the water absorption of the compounds containing 5, 10, and 15 volumes of barytes (Figure 1) and thermatomic carbon (Figure 2). The other pigments show similar results and therefore are not shown. The water-absorption data of the compounds containing 5, 10, and 15 volumes have been averaged to give a composite curve for each pigment. The control compound (Figure 3) containing no pigment shows a minimum water absorption at about the 80-minute cure for all periods of immersion. Whiting (Figure 4) and barytes (Figure 5) show a minimum water absorption at the 60-minute cure. The compound containing clay (Figure 6) shows higher water absorption on the overcures than on the undercures. After 30 days' immersion clay shows the lowest water absorption for the optimum cure. The compounds containing zinc oxide (Figure 7), thermatomic carbon

(Figure 8), and carbon black (Figure 9) show greater water absorption on the undercures than on the overcures. Thermatomic carbon after 1 day's immersion is an exception and shows higher water absorption on the overcures.

The optimum cure based on the time required to reach maximum tensile strength is 40 minutes on all compounds, with the exception of 10 and 15 volumes of zinc oxide and 5 volumes of carbon black, in which the optimum is 60 minutes. The optimum cure with 10 and 15 volumes of carbon black is 80 and 120 minutes, respectively. The minimum water absorption of the control without pigments is observed at the 80-minute cures. Zinc oxide after 7 and 30 days' immersion and carbon black after 1 and 7 days' also show a minimum at 80 minutes. The minimum water absorption on the other compounds is on the 60-minute cure, or a little past the optimum cure. Clay shows a minimum water absorption at the 20- to 40-minute cures.

A comparison of whiting, barytes, and the control (Figure 10) after 30 days' immersion shows but little difference in the undercures. Barytes at the optimum cure decreases the water absorption slightly, whereas whiting appears to exert no influence whatsoever on the water absorption of the optimum cure. In the overcures whiting gives the highest and the control the lowest water absorption. Both whiting and barytes increase the water absorption of the overcures compared with the control. The undercures show higher water absorption than the overcures.

Clay and zinc oxide (Figure 11) increase the water absorption of vulcanized rubber and show higher results than whiting or barytes. Zinc oxide shows the maximum water absorption at the undercures, which decreases to a minimum at the optimum cure after which it increases but slightly for the overcures. Clay shows the opposite behavior of zinc oxide, since it shows the greatest water absorption at the overcures. The water absorption of the undercures is not much higher than that of the optimum cure, after which the water absorption increases rather sharply.

Carbon black (Figure 12) does not appreciably affect the water absorption of the undercures, whereas thermatomic carbon decreases it. In the overcure carbon black shows slightly higher water absorption and thermatomic carbon slightly lower than the control.

In the undercures whiting, barytes, carbon black, and control show about the same water absorption, whereas clay and zinc oxide cause it to increase. In the overcures clay shows the highest water absorption, followed by zinc oxide and whiting. Carbon black and the control are very nearly the same and thermatomic carbon is lowest in both the under- and overcures. All the pigments, regardless of volume loading or time of immersion, decrease in water absorption to a minimum up to the optimum cure, after which the water absorption increases again with increasing time of cure.

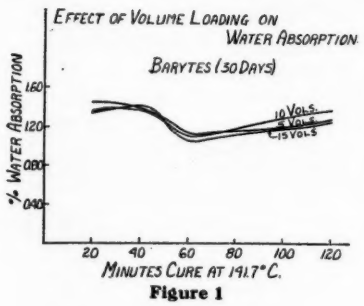
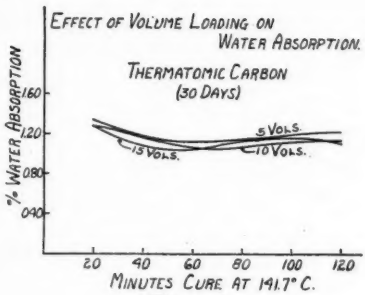


Figure 1



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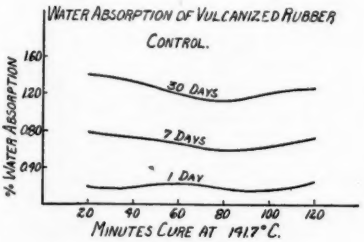


Figure 3

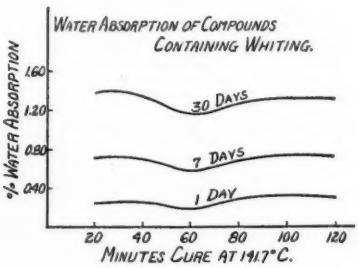


Figure 4

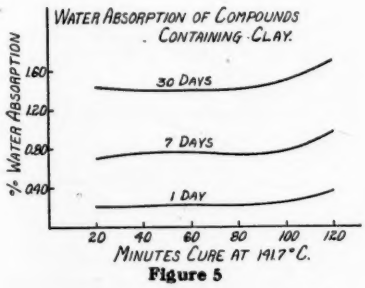


Figure 5

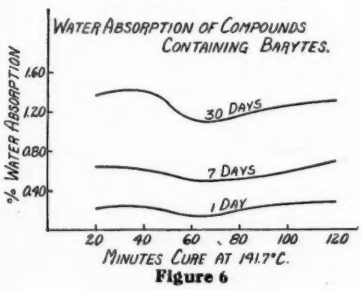


Figure 6

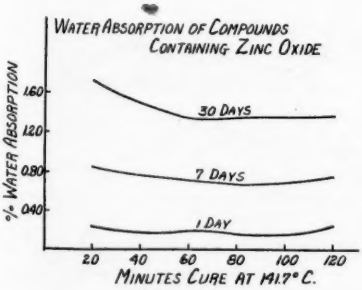


Figure 7

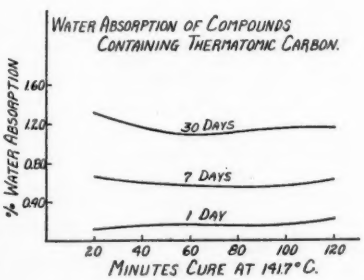
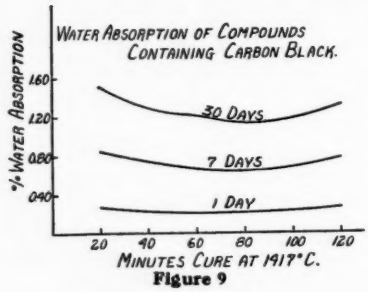


Figure 8



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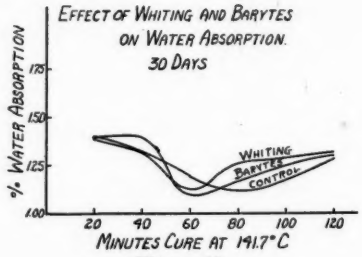


Figure 10

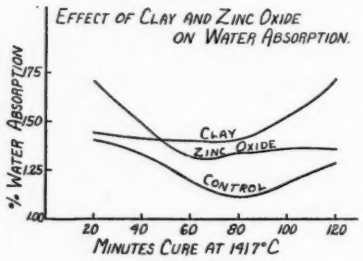


Figure 11

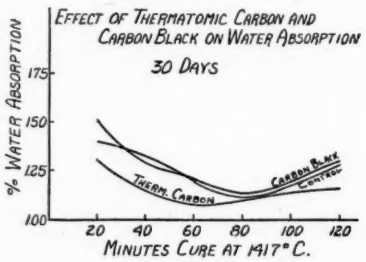


Figure 12

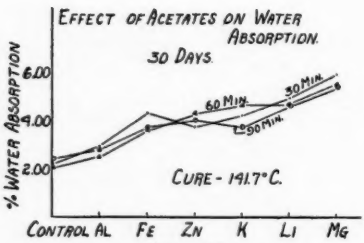


Figure 13

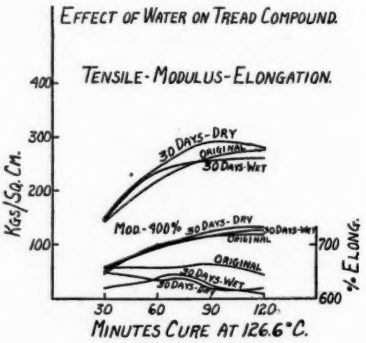


Figure 14

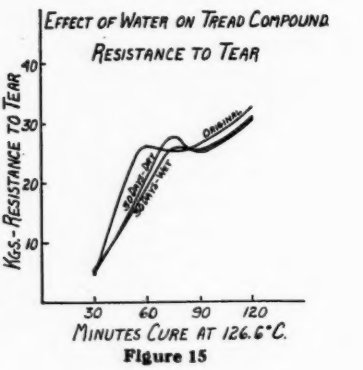


Figure 15

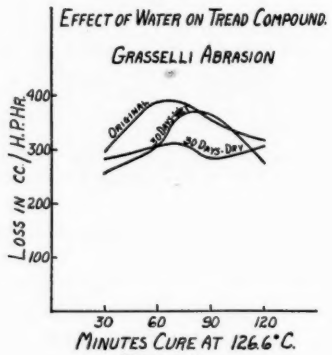


Figure 16

Effect of Metallic Acetates

To determine the effect of the presence in a rubber compound of various metallic acetates on water absorption, molecular equivalents were added to the following control recipe:

Pale crepe	100
Zinc oxide	5
Sulfur	5
Diphenylguanidine	0.75

The acetates were chosen in preference to the soluble salts of other acids, because acetic acid is used in the coagulation of rubber latex. The effect of water absorption on small amounts of acetates formed by the reaction of the traces of acetic acid with various compounding ingredients may be appreciated from these results. The acetates with the amount of each added to the above compound are as follows:

Aluminum acetate	1.62
Ferric acetate	4.0
Zinc acetate	2.37
Potassium acetate	1.0
Lithium acetate	1.02
Magnesium acetate	2.14

The percentage of water absorption for the 30-, 60-, and 90-minute cures is shown on Figure 13. The presence of the salt

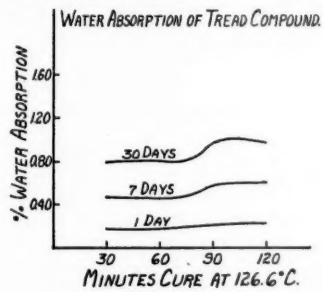


Figure 17

produces a marked increase in the water absorption. The order of increase in water absorption produced by these acetates is aluminum, iron, zinc, potassium, lithium, and magnesium.

Effect of Water on Tread Compounds

A study was made of the effect of water on the physical properties of a tread compound. For this purpose the following recipe was used:

Rubber	100
Zinc oxide	5
Stearic acid	4
Pine tar	3
Carbon black	40
Sulfur	3
Captax	0.6

Cures were obtained for 30, 60, 75, 90, and 120 minutes at 126.6° C. Standard 1/4-inch (6-mm.) test pieces were cut from each cure. Tests were obtained on the original com-

pound and on test pieces which had been immersed in water for 30 days and in one case tested immediately, and in the other after drying to constant weight in a desiccator over calcium chloride. These results are shown on Figure 14. The original tests are somewhat lower on the 30- and 60-minute cures, while on the 90- and 120-minute cures the tensile strength is somewhat higher. In the case of the samples dried after 30 days' immersion higher tensiles were obtained over the full range of cures. The modulus results are almost within experimental error, but again indicate higher results for the samples which were dried after 30 days' immersion. The highest elongation is obtained on the original compound.

The effect on the resistance to tear was also studied using

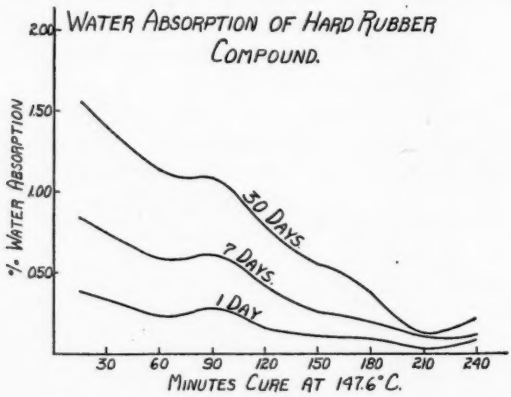


Figure 18

the Winkelmann tear test. These results are shown on Figure 15. The original compound, with the exception of an inconsistency on the 75-minute cure, appears to give the highest resistance to tear. The samples which were immersed in water check very closely and, with the exception of the points at the 75-minute cure, are somewhat lower than the original.

Observations made on the resistance to abrasion as determined on the Grasselli abrader indicate that the poorest results are obtained with the original compound. Water immersion causes an increase in the resistance to abrasion, although the longer cures are not very different from the results obtained with the original. The best resistance to abrasion is obtained on the samples which were immersed for 30 days and then dried before testing. (Figure 16)

Water-absorption tests obtained on the tread compound over a period of 30 days show maximum increase at the 90-minute optimum cure. This increase is more marked on the 7- and 30-day tests than the sample which was immersed for only 1 day (Figure 17). The fact that the water absorption

in 30 days does not exceed 1 per cent probably accounts for the small differences found in physical tests.

Water Absorption of a Hard-Rubber Compound

Water-absorption tests were made on a hard-rubber compound cured from 30 to 240 minutes at 147.6° C. at 30-minute intervals. The following recipe was used:

Smoked sheet	100
Sulfur	40

As would be expected, the percentage of water absorbed decreases with the time of cure. It is interesting to note, however, that after 210 minutes' curing there is a slight increase on all three curves (Figure 18).

Water Absorption of Reclaimed Rubber

In order to study the effect of water absorption on various types of reclaimed rubber, four representative grades were mixed with sulfur and cured for 15, 30, 45, 60, and 75 minutes at 141.7° C. Five parts of sulfur were added to 100 parts of alkali tube reclaim, neutral tube reclaim, and alkali whole-tire reclaim. Two parts of sulfur were added to 100 parts of shoe reclaim. The results are shown on Figure 19. The highest water absorption is obtained on the alkali tube reclaim. This decreases very rapidly until the optimum cure is reached, after which it remains almost constant. An alkali whole-tire reclaim has a much lower water absorption and does not show so great a variation over a range of cures. A neutral tube reclaim has very low water absorption and is almost constant over the entire range of cures. The lowest results are obtained with a shoe reclaim. It is quite evident from these results that the presence of residual alkali in a reclaim will result in an increased water absorption.

Summary of Results

1—Increased volume loading of any given pigment has very little effect on the water absorption of vulcanized rubber.

2—The water absorption of vulcanized rubber decreases with increasing time of cure reaching a minimum just after the optimum cure after which it increases again. The tread compound (Figure 18) is an exception because it shows the highest absorption at the optimum cures. The significant fact is that the water absorption of a compound varies over a range of cures.

3—Whiting and barytes increase the water absorption of overcured vulcanized rubber. Clay and zinc oxide show the greatest increase in water absorption. Carbon black has a very little effect whereas thermatomic carbon decreases water absorption.

4—The presence of salts such as metallic acetates increase water absorption. The presence of salts in compounding

ingredients will therefore affect the water absorption of the compound.

5—Immersion of a tread compound in water for 30 days does not appreciably affect the tensile strength or modulus—the elongation is decreased. The dried sample after 30 days' immersion shows higher tensile strength, no change in modulus and lower elongation, than the original.

6—Immersion of a tread compound has practically no effect on the resistance to tear. The resistance to abrasion of a sample immersed for 30 days is improved but shows even better results after drying.

7—Water absorption of a hard-rubber compound decreases with increasing time of cure.

8—Reclaimed rubbers show considerable variation in water absorption, depending on the type of reclaim, process of devulcanization, and materials which are present.

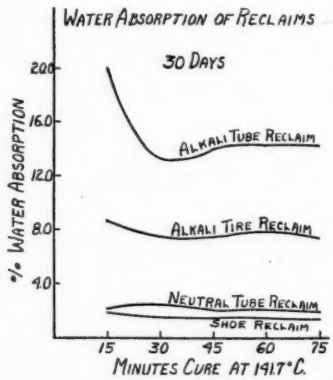


Figure 19

Conclusion

It seems advisable to await further experimental evidence before attempting a theoretical explanation of the results obtained. Further work should be done on the effect of softeners, accelerators, immersion at elevated temperatures, and source of pigment. Water absorption of the uncured compound is often important. Additional work will show whether the observations made here hold for different types of compounds containing combinations of pigments, reclaims, and accelerators. The fact that the control without pigment shows water absorption of about the same range as some of the pigments would indicate that water absorption when pigments are present is more or less independent of the tendency for these pigments to absorb moisture. Higher water absorption for the undercures may be due to porosity, the compound

becoming denser with increasing time of cure; the increase in water absorption after the optimum cure may be due to a chemical change of the protein during vulcanization.

A consideration of these problems will be helpful in the preparation of reclaims as well as rubber products subject to exposure to water and steam.

[Reprinted from the Journal of the American Chemical Society, Vol. 53, No. 1, page 203. January, 1931.]

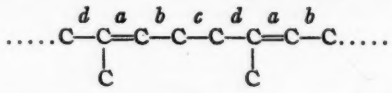
NATURAL AND SYNTHETIC RUBBER. VI. THE PYROLYSIS OF NATURAL RUBBER IN THE PRESENCE OF METALLIC OXIDES

THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

The first paper of this series[1] describes the influence of metals on the pyrolysis of natural rubber: it shows that the presence of a metal does not change the nature of the pyrolysis products, but affects their relative proportions. In this respect magnesium and zinc are most active. The fact that both zinc oxide and magnesium oxide influence the vulcanization process makes it desirable to study the influence of these compounds on the pyrolysis of rubber.

Experiments similar to these previously reported show that zinc oxide or magnesium oxide acts similarly to zinc or magnesium; zinc oxide has by far the stronger effect. Briefly the nature and proportion of pyrolysis products obtained with zinc oxide duplicate those obtained with magnesium, within experimental error.

Let the rubber molecule be represented by a long open-chain formula, and the various bonds of the chain be designated by letters



The relative numbers of ruptures at a, b, c and d during the pyrolysis of straight rubber have been computed from the data previously reported, and are represented by $a = 0$, $b = 0.6$, $c = 100$ and $d = 0.7$. However, a similar computation indicates that, in the case of rubber pyrolyzed with magnesium, the ruptures are as follows: $a = 0$, $b = 12.7$, $c = 100$ and $d = 12.1$. In both cases b equals d within experimental error.

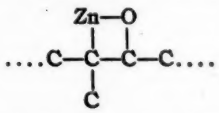
Since zinc oxide has the same effect as magnesium upon pyrolysis, it appears that its presence multiplies by about 17 the number of ruptures of the b- and d-bonds.

If d and b derive their strength from the fact that they are adjacent to the double bond a, it may be expected that any agent affecting the unsaturation of a will increase the similarity of d and b to c. If the agent be such as to remove entirely the unsaturated character of a, the bonds d, b

[1] Midgley and Henne, *J. Am. Chem. Soc.*, **51**, 1215 (1929).

and *c* might even become almost identical in strength, though complete identity would be prevented by the presence of the methyl side chains.

However, the formation of a chemical individual such as



with a zinc oxide molecule linked on the carbon chain by chemical valences does not seem to be supported by the facts: the pyrolysis products do not contain any compound formed by rupture of the chain at *a;* no oxygenated product is to be detected; and zinc oxide is not in the least reduced to the metal. Moreover, the seventh paper of this series shows that ruptures of *a* do occur in the pyrolysis of hard rubber where *a* is chemically saturated with sulfur.

Summary

Pale crepe rubber pyrolyzed in the presence of zinc oxide or magnesium oxide gives the same decomposition products as in the absence of the oxides, but in different proportions. This modification is attributed to an action of the oxides upon the double bonds of the rubber molecule.

COLUMBUS, OHIO

[Reprinted from Industrial and Engineering Chemistry, Vol. 22, No. 9, page 1004. September, 1930.]

Effect of Curing Temperature upon the Properties of a Rubber-Sulfur Mix[1]

C. R. Park[2]

THE GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

Data are presented covering a range of equivalent cures at six different temperatures on a stock consisting of rubber 100, sulfur 6.25. Neither the original properties nor the aging behavior show any definite trend with increase of curing temperature. Comparison is made of natural aging to artificial aging as conducted in the Geer oven and the Bierer and Davis bomb. The temperature coefficient of vulcanization is determined by three methods and found to be 2.50 per 10° C. or 1.64 per 10° F.

AT A meeting of the Rubber Division several years ago it was intimated that any given rubber mix would show much improved properties if the correct technical cure could be accomplished in a shorter time by any device, even that of raising the curing temperature. For example, if a stock reached its optimum properties in 3 hours at 140° C., its quality would be much improved by curing under the equivalent condition of 27 minutes at 162° C. It was this statement that suggested the present study.

Because of the immense amount of work involved it was considered inadvisable to try to cover the whole situation in one set of experiments. It seemed simpler to study, as thoroughly as possible, one particular mixing. The formula

[1] Received April 15, 1930. Presented before the Division of Rubber Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

[2] Present address, United Carbon Co., Charleston, W. Va.

chosen was rubber 100, sulfur 6.25, since this would eliminate the variable effects of accelerators and other compounding ingredients and reduce the problem to its simplest terms. It will be understood, therefore, that the conclusions drawn are meant to apply only to the mixture in question.

Experimental Procedure

The experimental procedure was made to conform to the recommendations of the Physical Testing Committee (*5*); the only exception being that certain of the tensile tests were made on the Goodyear testing machine rather than on the testing machine generally used. The die used for this machine is 1 cm. in width. Care was taken throughout that samples which were compared in any way were tested under the same conditions.

The stock mentioned above was a factory stock and the rubber used was always made up from a mixture of first quality sheet and crepe. So much time has elapsed between the start of the experiments and the assembly of the data that the exact proportions of these rubbers used in this particular batch have been lost from the record.

Table I—Curing Periods

No.	135.5° C.	141.5° C.	147.5° C.	152.5° C.	157.5° C.	162° C.
	Minutes	*Minutes*	*Minutes*	*Minutes*	*Minutes*	*Minutes*
1	300	150	89	46	34	21
2	330	165	97	52	38	24
3	360	180	105	58	41	27
4	390	195	113	64	45	30

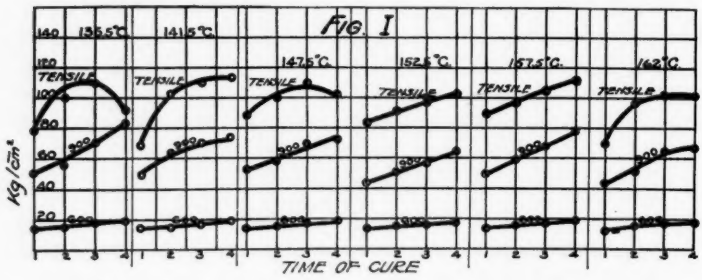
Sufficient stock for all the experimental work was taken from a single factory-milled batch. In order to insure uniformity, this stock was blended, without excessive milling, upon a 20-inch (51-cm.) experimental mill. The whole batch was then sheeted to the proper thickness, for curing and testing. The cures shown in Table I were established as being as nearly equivalent as it was possible to obtain. Judgment was based upon stress-strain behavior and an examination of the cured stocks by such hand methods as were traditional in this laboratory—e. g., the resistance to tear and appearance of the torn stock. The selection of cures was facilitated by a long period of practical experience with the particular stock in factory curing. Subsequent data seem to reflect well on the selection. Sufficient sheets were then cured according to the schedule given in Table I to furnish material for original and age tests.

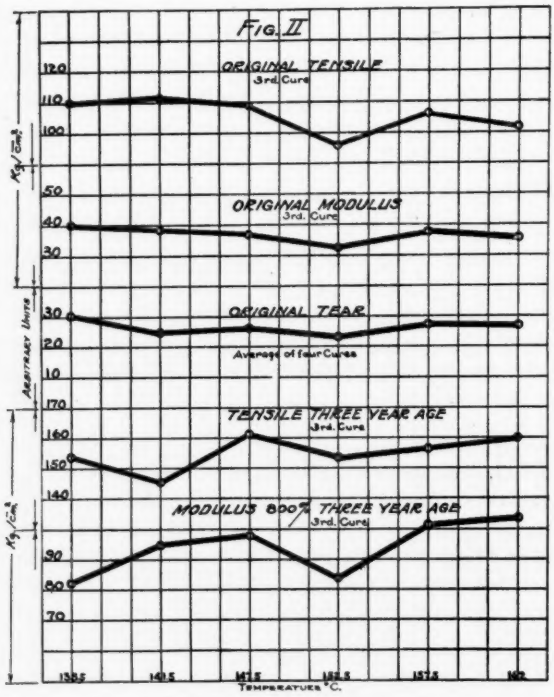
Physical Properties

The physical data in substantiation of the choice of curing ranges are set forth in Figure I. The original stress-strain properties are compared in such a way as to eliminate the awkwardness of the different periods of time used in curing. In other words, the third has been chosen as the optimum cure and the two undercures and the overcure have been

plotted in all cases at equal distances below and above the optimum. Although done for convenience only, this device serves to express all times as percentages of the optimum time. The optimum time, in this case, is defined as the correct time to produce the approved factory cure.

Those acquainted with stocks of this type will recognize the difficulties in making tensile tests. The stock is rather

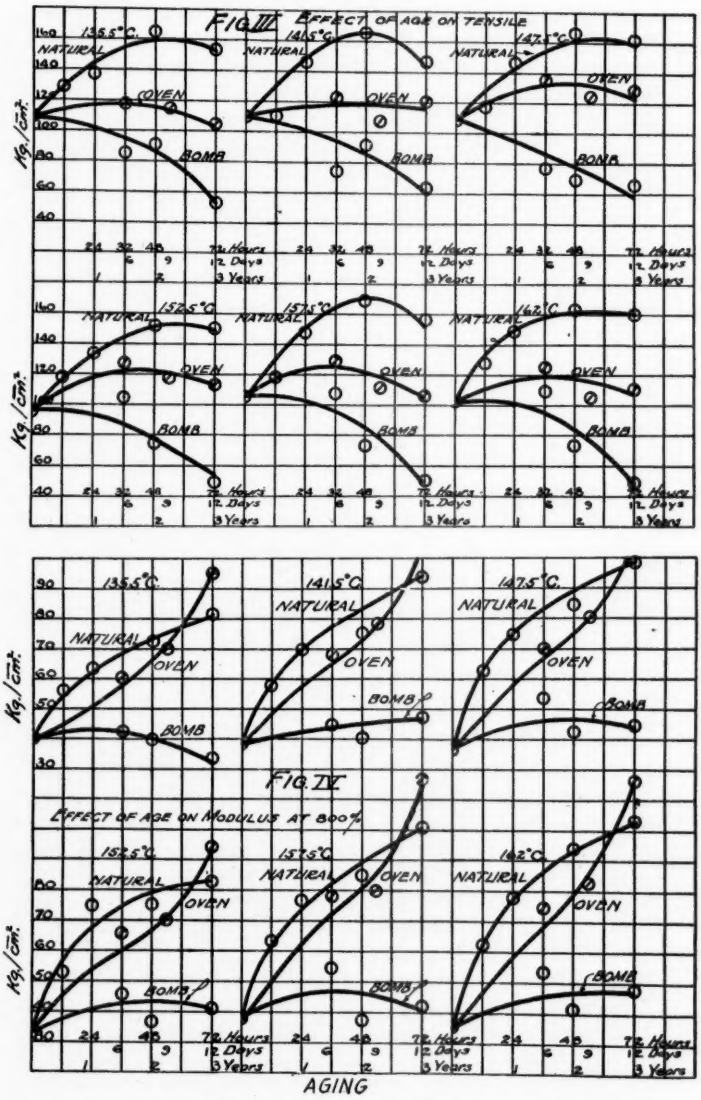




tender and the variation in tensile break greater than for most gum stocks. Modulus data are consequently more reliable than tensile data. All tests are the average of two strips.

An examination of Figure I will show that the samples cured at the various temperatures are reasonably near each

other in their physical properties, especially modulus. It is the writer's judgment, from a study of these data, that there is no definite trend and that the differences exhibited are only those which might be expected among six series of cures made at the same temperature but on different days. The results

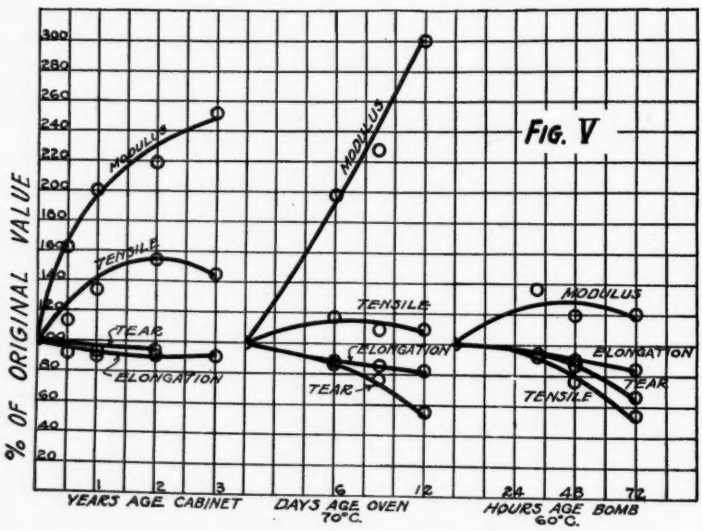


are repeated, together with some additional material in Figure II. The tear data given are arbitrary figures which represent comparative energy consumed in separating a given surface area. It happens, in the case of tensile and modulus figures,

that there appears to be a slight downward trend. It seems that this effect is caused entirely by random variation, since the same trend is not present in a plot of some of the other cures, notably the fourth of Figure I.

Aging Behavior

A fairly extensive study has been made of the aging behavior. Samples were aged for 6, 12, 24, and 36 months in a cabinet at room temperature, averaging probably 25° C.; for 6, 9, and 12 days in the Geer oven at 70° C.; and for 32, 48, and 72 hours in the Bierer-Davis bomb at 60° C. The effect of these aging treatments upon the tensile and modulous is shown in Figures III and IV. The points plotted in these figures are for the third cure in each series and are read from curves such as those shown in Figure I. The points given are



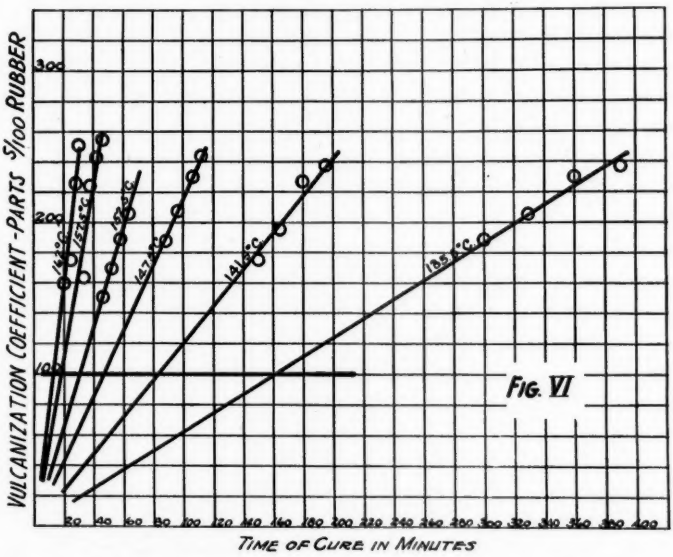
therefore supported by a large number of data. The bomb-aging curves are the least reliable of the three, since the capacity of one bomb was insufficient to accommodate, at one time, all the specimens tested. The stocks were aged in such a way as to give the best possible comparison of stocks cured at different temperatures. The comparison between the 32-, 48-, and 72-hour points is not very good and it is noticeable that these points do not fall on a smooth curve.

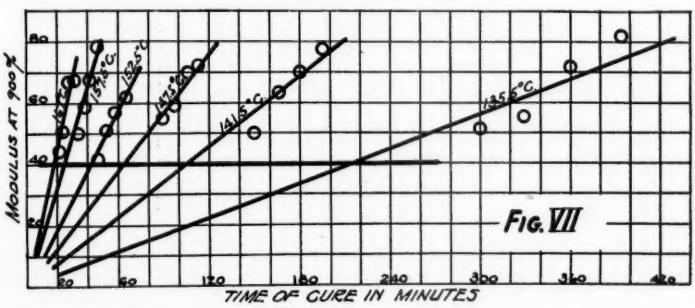
Aside from random variation, the temperature of cure seems to have had no effect on the aging behavior.

The behavior under the three aging conditions indicates that the effects produced in the sample are not only quantitatively but qualitatively different. While admitting the practical value of accelerated age tests, especially when backed up by considerable experience, the writer cannot but conclude that there is a very patent difference between the proc-

esses of change induced by normal aging and by the accelerated tests here used.

The curves shown in Figure III are typical of extensive tests made, over a period of years, on this type of stock. It has been the writer's unvarying experience that, while the tensile strength of this stock increased decidedly upon natural aging, a similar increase did not take place at any period during accelerated aging by either one of the methods under consideration. Too little information is available to warrant





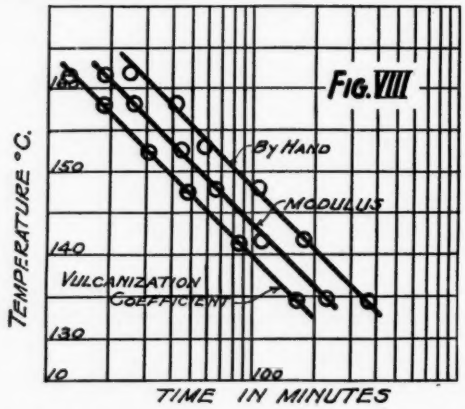
even a suggestion as to the cause of differences between the various methods of aging; nevertheless, it is worth while again to point out these differences which have been mentioned in previous papers (*1*, *6*, *7*). Further data relative to the above discussion are shown in Figure V, where the grand average behavior of the six sets is shown under each aging treatment.

The data so far presented do not enable one to draw any broad generalization as to the effect of curing temperature. They do point to the fact that the simple rubber-sulfur mix

gives, within experimental error, the same result at any temperature, within the range tried, provided equivalent times of cure are used. It follows that improved physical properties which are reported with lower temperature cures, are caused by the introduction of other compounding ingredients, accelerators probably playing the most important part.

Temperature Coefficient of Vulcanization

Inasmuch as the data were at hand, the temperature coefficient of vulcanization has been calculated. In Figure VI the vulcanization coefficients have been plotted against the time of cure for each temperature. From this plot the times to reach a vulcanization coefficient of 1 have been read and plotted against the corresponding temperatures in Figure VIII. In Figure VII the modulus at 800 per cent has been plotted against the time of cure for each temperature. From this plot the times to reach a modulus of 40 have been read off



and plotted against the corresponding temperatures in Figure VIII.

In Figure VIII are also plotted from Table I the times of cure to reach the so-called optimum conditions. The parallelism between these three lines makes it again evident that the curing ranges in Table I were well chosen. The temperature coefficient, as calculated from these curves, is 2.50 per 10° C., or 164 per 10° F. This value is in fair agreement with previous determinations (*2*, *3*, *4*).

Conclusions

1—Within experimental error, within the range of temperature and in the case of the mix under consideration, the temperature of cure has no effect on the quality of the vulcanized stock.

2—Certain unexplained differences exist in the results obtained by various methods of aging.

3—The temperature coefficient of vulcanization is 2.50 per 10° C.

Acknowledgment

Thanks are due R. P. Dinsmore, of the Goodyear Tire and Rubber Company, for permission to publish this material.

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Behavior of Antioxidants in Rubber Stocks Containing Copper[1]

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SYSTEMS which are sensitive to negative catalysts are usually sensitive to positive catalysts (*10*). In many cases significant experiments can be carried out by introducing both types simultaneously into the same system. In this paper the behavior of antioxidants in vulcanized rubber stocks containing copper stearate is discussed, copper stearate being a vigorous accelerator of the deterioration of rubber through oxidation (*2* to *9*, *11*, *12*, *13*, *15* to *21*). In the experiments about to be reported a number of antioxidants, including representatives of several types (Table I), have been tested in two tread stocks (A and B) containing a definite amount of copper stearate.

Table I—Representatives of Types of Antioxidants Used

TYPE	COMPOUNDS
Hybrocarbons	Paraffin, m. p. 56° C. Paraffin, m. p. 68° C.
Primary aromatic amine	4,4′-Diaminodiphenylmethane
Aliphatic aromatic secondary amine	*n*,*n*′-Di-*p*-tolyl-1,2-ethylenediamine
Secondary aromatic amines	Phenyl-β-naphthylamine Phenyl-α-naphthylamine *n*,*n*′-Diphenyl-*p*-phenylenediamine *n*,*n*′-Di-β-naphthyl-*p*-phenylenediamine
Aldehydeamine	Aldol-α-naphthylamine
Tetraarylhydrazine	Tetraphenylhydrazine

The effect of variations in concentration of phenyl-β-naphthylamine has been determined in stock A. The activity of phenyl-β-naphthylamine, both in the presence and in the absence of copper stearate, was investigated for

[1] Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

a series of mixes comprising two tread compounds (A and B), a high zinc oxide compound (C), and a high-gum compound (D). The concentration of copper stearate was kept constant for each series.

In subsequent tables copper-free compounds will be listed as A, B, etc., and the corresponding stocks containing copper as A (Cu), B (Cu), etc.

Table II—Composition of Rubber Stocks

	Stock A	Stock B	Stock C	Stock D
Rubber	100.0	100.0	100.0	100.0
Sulfur	3.5	5.6	3.25	2.15
Zinc oxide	9.5	28.0	86.0	3.22
Gas black	43.0	37.0	....	....
Pigment	....	....	12.2	....
Softener	15.5	15.0	1.0	0.86
Accelerator	D.P.G. 1.04	Hexa 0.75	A 16 1.63	Captax 1.07
	172.54	186.35	204.08	107.30

The copper stearate used contained 15.8 per cent of copper and showed the presence of considerable copper carbonate.

Copper stearate was used in a concentration of 0.2 per cent on the stocks listed in Table III of series A (Cu). In all other tests with series A (Cu), B (Cu), C (Cu), and D (Cu), 0.1 per cent on the compound was used.

Relative Activity of Antioxidants

Table III for tread stock A shows that the order of activity of the antioxidants is substantially the same in the presence of copper as in its absence. In both cases the secondary aromatic amine, *n, n'*-diphenyl-*p*-phenylenediamine, is the best in the series. Tetraphenylhydrazine and aldol-α-naphthylamine are of about the same value in the oven, while the bomb aging shows the former to be of greater benefit both in the presence and in the absence of copper. The diprimary aromatic amine, although of some benefit in the absence of copper, confers only slight resistance to oxidation when copper is present. In neither case are the paraffin hydrocarbons beneficial. The 7-day oven tests show a fair degree of correlation with natural aging. Deterioration during the 48-hour bomb tests had proceeded too far for comparison.

The data in Table IV show that the relative activities of the antioxidants, in the oven, remain practically unchanged when copper is introduced into the compounds. The results from the bomb for the stocks containing copper form a less well-defined series than those obtained from oven tests. However, the secondary aromatic amines are of outstanding effectiveness.

Phenyl-β-naphthylamine is a valuable ingredient in the high zinc oxide stock, even though the compound has very good age-resisting properties in the absence of antioxidant, as shown in Table V. The beneficial effect of phenyl-β-naphthylamine is marked in the bomb in the presence of copper, and is noticeable in the oven.

Table III—Tread Stocks A and A (Cu)

Cure, 45 minutes at 146° C. (295° F.)

Antioxidant (0.5% on batch)	Original				Geer Oven for 7 Days at 70° C.				Bierer Bomb for 48 Hours at 70° C. and 21.1 kg./sq. cm. (300 lbs./sq. in.) of Oxygen				Natural Aging in Darkness			
	A		A (Cu)		A		A (Cu)		A		A (Cu)		A 14 months[b]		A (Cu) 8 months	
	Tens.[a]	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.
	Kg./cm.²	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%
None	261 (3710)	710	255 (3630)	700	170 (2420)	570	141 (2010)	550	87 (1240)	500	Melted		229 (3260)	630	174 (2470)	580
Paraffin, m. p. 68° C.	...	...	259 (3690)	700	...	...	138 (1970)	550	...	...	Melted		...	...	164 (2330)	580
Paraffin, m. p. 56° C.	...	...	257 (3660)	700	...	...	148 (2110)	550	...	...	Melted		...	...	167 (2380)	570
p,p'-Diaminodiphenylmethane	264 (3760)	640	274 (3900)	660	221 (3140)	530	171 (2430)	480	127 (1810)	480	Melted		232 (3290)	640	210 (2990)	530
n,n'-Diphenyl-*p*-phenylenediamine	269 (3830)	670	256 (3650)	690	252 (3590)	600	248 (3530)	640	227 (3230)	600	79 (1120)	480	256 (3640)	680	250 (3560)	660
Aldol-α-naphthylamine	249 (3550)	680	247 (3520)	700	212 (3020)	650	190 (2700)	620	165 (2350)	660	Cracked		236 (3350)	670	220 (3120)	630
Tetraphenylhydrazine	260 (3700)	730	239 (3400)	710	210 (2980)	660	176 (2500)	610	200 (2850)	630	51 (720)	390	...	...	...	...

[a] Numbers in parentheses refer to tensile in pounds per square inch.

[b] Aging data given in this column were adopted from another series of experiments in which the concentration of the antioxidant was 0.2 per cent on the batch in each case. That for 8 months' natural aging of stock A is not available.

Table IV—Poor Aging Tread Stocks B and B (Cu)
Cure, 45 minutes at 144° C. (292° F.)

Antioxidant (0.5% used)	Original				Geer Oven for 7 Days				Bierer Bomb for 48 Hours at 70° C. and 21.1 kg./sq. cm. (300 lbs./sq. in.)			
	B		B (Cu)		B		B (Cu)		B		B (Cu)	
	Tens.[a]	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.
	Kg./cm.²	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%
None	261 (3710)	610	264 (3760)	590	98 (1390)	345	102 (1450)	330	49 (690)	290	Resinified	
n,n'-Di-*p*-tolyl-1,2-ethylenediamine	...	...	266 (3790)	610	...	...	114 (1620)	345	...	...	39 (550)	190
n,n'-Diphenyl-*p*-phenylenediamine	269 (3830)	670	253 (3600)	610	252 (3590)	600	215 (3060)	605	227 (3230)	605	179 (2540)	560
n,n'-*ββ*-naphthyl-*p*-phenylenediamine	270 (3840)	640	253 (3600)	640	251 (3570)	545	202 (2880)	580	204 (2900)	580	145 (2060)	535
Phenyl-*β*-naphthylamine	240 (3420)	620	278 (3960)	610	188 (2680)	540	183 (2600)	500	176 (2510)	535	155 (2200)	550
Phenyl-*α*-naphthylamine	273 (3890)	630	268 (3810)	620	191 (2720)	515	197 (2800)	500	185 (2610)	570	181 (2570)	580
Aldol-*α*-naphthylamine	247 (3510)	700	269 (3830)	630	189 (2690)	540	150 (2130)	420	145 (2070)	560	27 (390)	130

[a] Numbers in parentheses refer to tensile in pounds per square inch.

Table V—Phenyl-β-Naphthylamine in High Zinc Oxide Stocks C and C (Cu)
Cure, 20 minutes at 142° C. (287° F.)

Concn. of Anti-oxidant	Original				Geer Oven for 7 Days				Geer Oven for 14 Days				Bierer Bomb for 24 Hours				Bierer Bomb for 48 Hours			
	C		C (Cu)		C		C (Cu)		C		C (Cu)		C		C (Cu)		C		C (Cu)	
	Tens.[a]	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.
%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%	*Kg./cm.²*	%
0.0	227 (3210)	700	235 (3350)	700	221 (3140)	690	186 (2640)	670	168 (2390)	650	143 (2070)	650	222 (3160)	670	Melted		170 (2421)	620	Melted	
0.5	230 (3280)	710	246 (3500)	720	222 (3170)	680	209 (2960)	700	195 (2790)	680	166 (2340)	650	230 (3280)	670	171 (2450)	680	223 (3180)	680	86 (1220)	640

[a] Numbers in parentheses are tensile in pounds per square inch.

Table VI—Phenyl-β-Naphthylamine in Pure-Gum Stocks D and D (Cu)

Cure, 20 minutes at 144° C. (292° F.)

Concn. of Anti-oxidant	Original				Geer Oven for 7 Days				Bierer Bomb for 48 Hours			
	D		D (Cu)		D		D (Cu)		D		D (Cu)	
	Tens.[a]	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.
%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%
0.0	256 (3640)	800	248 (3530)	790	239 (3400)	720	195 (2770)	705	240 (3410)	780	175 (2490)	740
0.5	249 (3540)	780	249 (3540)	660	252 (3580)	730	214 (3050)	640	248 (3520)	735	219 (3110)	730

[a] Numbers in parentheses refer to tensile in pounds per square inch.

Table VII—Variation of Phenyl-β-Naphthylamine Concentration in Tread Stocks A and A (Cu)

Cure, 45 minutes at 144° C. (292° F.)

Concn. of Anti-oxidant	Original				Geer Oven for 14 Days				Bierer Bomb for 24 Hours				Bierer Bomb for 48 Hours			
	A		A (Cu)		A		A (Cu)		A		A (Cu)		A		A (Cu)	
	Tens.[a]	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.
%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%	*Kg./cm.*²	%
0.0	239 (3400)	720	259 (3680)	735	103 (1460)	500	[120 (1700)]	460	118 (1680)	590	28 (398)	350	72 (1030)	490	20 (280)	110
0.1	253 (3600)	720	238 (3390)	730	124 (1770)	530	105 (1490)	510	160 (2280)	620	89 (1270)	570	132 (1870)	570	32 (450)	350
0.2	258 (3670)	740	247 (3520)	740	143 (2030)	540	115 (1640)	510	185 (2630)	640	107 (1520)	570	159 (2260)	600	42 (600)	410
0.5	262 (3720)	700	240 (3420)	720	170 (2420)	580	155 (2170)	590	194 (2760)	620	154 (2160)	650	186 (2650)	630	75 (1070)	530
1.0	259 (3690)	710	234 (3330)	710	185 (2630)	570	173 (2460)	580	199 (2830)	630	169 (2400)	660	190 (2700)	620	96 (1360)	570
2.0	235 (3350)	730	244 (3470)	750	191 (2720)	610	179 (2550)	620	204 (2900)	690	171 (2440)	650	190 (2700)	620	101 (1440)	570
5.0	232 (3300)	750	216 (3080)	740	188 (2670)	660	166 (2360)	630	207 (2920)	690	159 (2270)	690	191 (2720)	680	116 (1650)	640

[a] Numbers in parentheses refer to tensile in pounds per square inch.

The pure-gum compound used to obtain the data in Table VI aged exceptionally well. Nevertheless, phenyl-β-naphthylamine brings about increased resistance to deterioration by copper.

Effect of Increasing Concentration of Antioxidant

Previous experience in certain stocks with phenyl-β-naphthylamine has brought out the fact that increasing the concentration of antioxidant beyond about 1 per cent produces relatively small increases in age-resisting properties. It was desired to study the effect of copper on this phenomenon. The results reported in Table VII are similar to those previously obtained except in the case of the 48-hour bomb aging of stocks containing copper, where oxidation was very severe. In this case age-resisting properties were increased slightly by increased proportions of the antioxidant.

Application of Bailey's Theory of Inhibition

It is worthwhile to call attention here to the work of Bailey (*1*), who studied the esterification of ethyl alcohol by acetic acid and likewise the oxidation of benzaldehyde. Bailey believes that these reactions are in part initiated at interfaces and that the effectiveness of certain inhibitors involves their preferential adsorption at these interfaces. Whether or not the effect of rubber antioxidants involves similar mechanism, the activity-concentration curves for the secondary aromatic amine type of antioxidant resemble the corresponding activity concentration curves obtained by Bailey. The curves for 48-hour bomb aging for phenyl-β-naphthylamine are given in Figure 1, assuming that aging is due chiefly to oxidation and can be measured by the drop in tensile (Table VII). The presence of copper apparently does not influence the type of curve obtained. If Bailey's theory of inhibition applies to the behavior of this antioxidant in rubber, it means that high concentrations of phenyl-β-naphthylamine exist at active surfaces or points in the rubber compound where oxidation is initiated (*9*). Evidence (*14*) has been presented to show that phenyl-β-naphthylamine is chemically changed during the aging process. Probably it is oxidized as it exerts its retarding action which, owing to lack of data, can be accounted for by a number of theories. The active-interface theory is substantiated by flexure-cracking experiments. Flexure cracking probably starts at interfaces where the bonds between phases are weakest. During flexing oxidation should occur there, and it has been found that many antioxidants have a pronounced effect in retarding flexure cracking. For instance, the presence of 0.5 per cent of phenyl-β-naphthylamine will more than double the life of many tread compounds, as estimated by tests carried out in this laboratory. Materials of similar physical properties but which are not antioxidants do not retard the rate of cracking. The effect of

the copper stearate[2] might be explained as being due to an increase in the amount of active interface or to an increase in the activity of the interface normally present. In any case the fact that certain antioxidants are so effective in retarding the action of copper stearate substantiates the

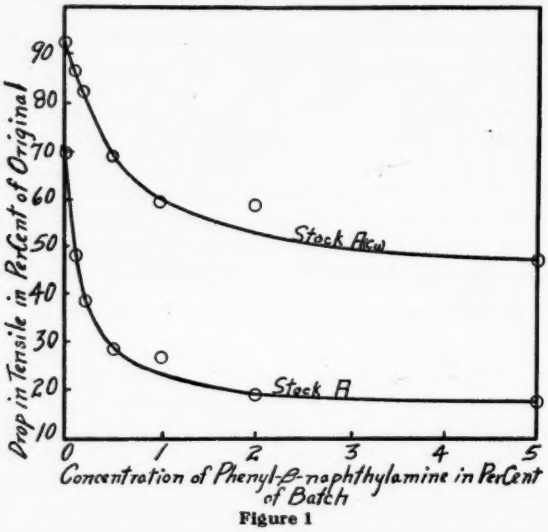

Figure 1

evidence previously found that copper compounds accelerate the oxidation of rubber. Phenyl-β-naphthylamine has been an ideal antioxidant for this study, since it fluxes well with rubber and has slight effect on the aging factors other than oxidation.

Conclusion

It is difficult, when comparing effects of various antioxidants in a stock, to distinguish clearly their relative influence on the physical properties of the stock during the aging period. This difficulty arises because of the difference in effect on cure of various age resisters, in acting as activators, or stiffeners, or softeners. It is suggested, in order to measure the relative degrees of protection against oxidation conferred by various age resisters, that copper compounds be added. This should be of valuable assistance in segregating the oxidation factor of aging, since oxidation is thereby greatly accelerated.

An examination of the data obtained makes it seem probable that wherever rubber is likely to be subjected to severe oxidation due to catalysis by copper or copper compounds, properly chosen antioxidants will be of practical value. Such a situation may be found where brass comes in contact with rubber. Other instances will be met in technical experience.

[2] See reference (9) for Kirchhof's views of the mechanism of the action of copper salts.

Summary

(1) Deterioration accelerated by copper in a high-grade tread stock, a low-grade tread stock, a high zinc oxide bus-tube stock, and a pure-gum stock has been found to be effectively retarded by the use of suitable antioxidants.

(2) Secondary aromatic amines have been found to be much more effective than other antioxidants, in tread stocks, for retarding deterioration due to copper.

(3) The degree of protection afforded to rubber compounds containing copper by the use of certain antioxidants, notably secondary aromatic amines, is sufficiently high to make their addition of practical importance.

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Surface Application of Age Resisters to Cured Rubber *vs.* Mill Incorporation Prior to Cure[1]

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The protection afforded against accelerated aging was determined by applying representative hydrocarbons, aldehydeamines, phenols, primary amines, alkarylamines, diarylamines, and thiazines to tread stock. A comparison of surface application *vs.* mill incorporation was made in a high-grade non-blooming tread, a high zinc oxide blooming tread, a white mechanical, and a pure-gum stock.

For most purposes mill incorporation is preferable to surface application of age resisters to rubber, although surface application will retard deterioration even after it has once commenced. No inversion of the protective action has been noted from the results of many tests with nitrogenous age resisters. It therefore appears that age resisters of the amine types are dependable for assuring protection to rubber articles.

THE idea that various oils or chemical solutions may be applied to the surface of rubber to retard deterioration has long been recognized. Kreussler and Budde (*5*) in 1881 mentioned and patented the application of paraffin or paraffin oils for preserving cured rubber articles. In 1898 it was mentioned anonymously (*1*) that the useful life of rubber articles might be prolonged by washing them in soda soap and immersing in ammonium carbonate solution, al-

[1] Received April 15, 1930. Presented before the Division of Rubber Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

though better results were to be obtained by applying creosote or carbolic acid solution. Wolfgang and Walter Ostwald (*11*) in 1909 recommended the preservation of rubber by painting, swelling, or spraying with liquids or solutions of "neutral and basic aromatic nitrogen compounds, neutral or basic heterocyclic substances and alkaloids, either alone or mixed." The application of terpineol or emulsions thereof was suggested by Beyer (*2*) in 1911 as a means of preserving the elasticity of rubber. In 1919 Zertuche (*14*) applied to rubber, as a preservative, the juices of certain desert shrubs such as mesquite.

Paints made from various oils, waxes, tars, resins, or pitches have for many years been used to improve the appearance and possibly to retard the deterioration of cured rubber goods. Reference to the patents granted on these paints shows to what extremes the idea of painting was carried. One example is a composition of tar, pitch, resin, rubber cement, fish glue, and glycerol suggested by Thierfelder and Schmaelzle (*12*) for preserving treads of tires.

Moureu and Dufraisse (*9*) in 1922 patented the surface application of phenols to rubber and other oxidizable materials as a means of preventing their deterioration. Martin (*7*) mixed aniline or other amines with cottonseed oil and applied the mixture to tires, hose, etc., for lengthening their useful life. Cadwell (*3*) investigated a wide range of organic compounds which absorb activated oxygen. He reported solutions of aldehydeamines, *p*-aminophenol hydrochloride, diphenylnitrosamine, *p*-nitrosodiphenylamine, and numerous others as being of value for preserving rubber when applied to the surface of cured articles.

Recently Fiedler (*4*) has patented the preservation of rubber articles by painting them with mixtures such as glycerol and benzaldehyde or glucose and phenylhydrazine, either alone or in rubber cements. A composition consisting of a mixture of glycerol and drying oil was patented by Kurtz (*6*) to be used for preserving the surface of air bags.

The Bureau of Standards (*13*) carried out tests in which five different age resisters were applied to the surface of articles such as surgeons' gloves, by dipping them in a benzene-alcohol solution of the material. In every case the results were beneficial.

Moureu, Dufraisse, and Lotte (*10*) have stressed the idea that "antioxygens" are extremely irregular in their protective action. Referring to the surface method of applying "antioxygens" they have stated: "There is a danger, therefore, if one does not take all the necessary precautions, of hastening the loss of rubber objects in trying to protect them." They have tabulated the excessive variation of the protective action of hydroquinone. Varying results from almost perfect protection to fair protection were obtained when an ether solution was used, but an acetone solution caused accelerated deterioration.

Experimental

The results obtained and conclusions drawn by Moureu, Dufraisse, and Lotte are so at variance with general observations which the writers have made using age resisters typical of classes of materials now being marketed for rubber compositions that it has seemed desirable to compare more fully the method of surface application with mill incorporation prior to cure.

The method of surface application does not seem to have been extensively practiced. The purpose of this article is to show that this lack of practical application is due, not to any inherent defect in the method, but rather to processing difficulties and to less effective action.

The comparison has been extended and has included a large number of preservatives.[2] Certain typical results are presented because of their general interest.

Figure 1 shows in chart form the relative protection against aging afforded to a high zinc oxide, blooming tread stock by twenty age resisters when 0.5 per cent was incorporated prior to cure and when test strips of the stock were soaked for 10 minutes in 5 gram per 100-cc. solutions of the age resisters in acetone or benzene prior to aging. Accelerated aging tests were run in the Bierer bomb at 70° C. under 21.1 kg. per sq. cm. (300 lbs. per sq. in.) of oxygen or in the Geer oven at 70° C. in a continually renewed current of air.

The upper bar of each pair represents the tensile strength of test pieces in which 0.5 per cent of age resister was incorporated on the mill prior to cure while the lower bar shows the tensile strength of the samples to which the age resister was applied to the surface of the cured stock prior to aging.

Figure 2 shows a similar comparison of ten materials in a high-grade non-blooming tread stock.

Order of Activity of Age Resisters

The results show that the order of activity of the age resisters is essentially the same in both stocks whether they are applied to the surface or milled into the rubber.

The results shown in the figures are also typical of, and agree with, the order of effectiveness established by more extensive studies with tread stocks. Ceresin as a representative of a class of waxes which protect stretched rubber samples from checking in the sunlight is without effect in retarding oxygen or heat deterioration. Phenols are comparatively weak in their action, the polyhydroxy compounds being more active than the monohydroxy while the amine salts of either show considerably more activity. Phenols containing two or more ring structures are in general more active than those containing only one. Primary amines show relatively weak protective action in the oxygen bomb yet are fairly efficient

[2] Many of the materials tested in this investigation are the subjects of patents issued or pending and cannot, therefore, be used commercially in rubber except under license from the assignees.

Table I—A Comparison of Accelerated Aging Tests of a High Zinc Oxide Tread Stock to Which Pyrogallol, Aniline, or Their Mutual Salt Was Added Prior to Cure

	Original			After 48 Hours at 70° C. 21.1 kg. per sq. cm. Oxygen			After 7 Days in Geer Oven at 70° C.		
	Ultimate tensile		Elong. at break	Ultimate tensile		Elong. at break	Ultimate tensile		Elong. at break
	Kg. per sq. cm.	*Lbs. per sq. in.*	%	*Kg. per sq. cm.*	*Lbs. per sq. in.*	%	*Kg. per sq. cm.*	*Lbs. per sq. in.*	%
Control	238	3385	668	52	742	323	126	1789	500
0.5% Pyrogallol	226	3224	603	49	698	277	114	1624	395
0.5% Pyrogallol aniline (1:1 mol)	263	3742	660	77	1089	480	191	2725	542
0.5% Aniline	253	3604	647	69	977	373	154	2191	525

when tested in the Geer oven. Monoprimary amines show low activity while the di and poly primary amines are considerably more active. The combination of a hydroxy and a primary amino group in a single molecule gives an effect which is more than the additive effect of the two groups. This is of interest in the light of the increased activity of phenolamine salts. Certain aldehydeamines show fair ac-

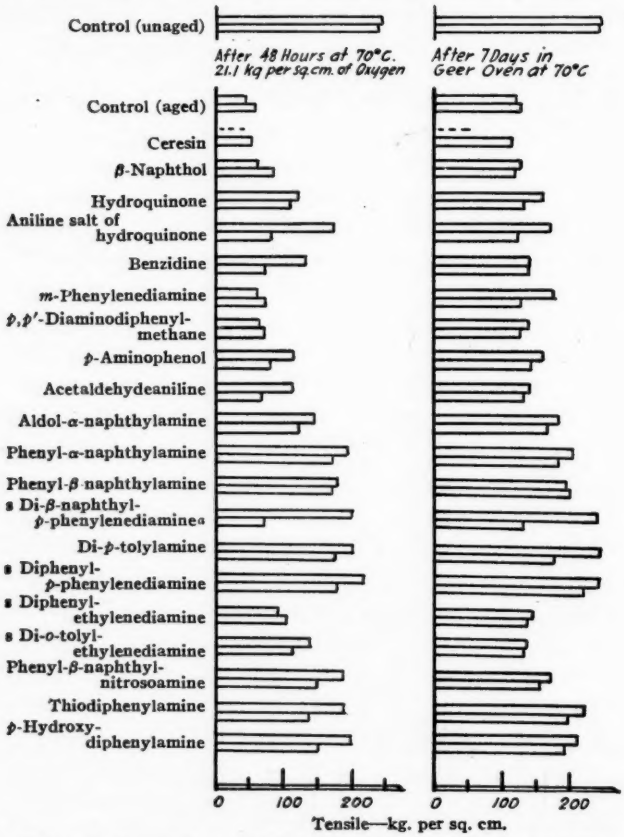

Figure 1—Comparison of Mill Incorporation and Surface Application of Various Materials for Retarding Deterioration of a High Zinc Oxide, Blooming Tread Stock

[a] A saturated solution in acetone was used. This was much more dilute than 5 per cent.

tivity, especially toward heat deterioration. Aryl secondary amines as a class are of considerable commercial importance. In general they are good age resisters and also retard cracking upon repeated flexing. Alkarylamines are of mild activity, although their effect is enhanced by putting two secondary amino groups into the same molecule. Diarylamines show higher activity. The activity increases as substituent groups are introduced into the diphenylamine molecule. Thus,

ditolylamine and phenylnaphthylamine have higher activity than the unsubstituted diphenylamine. The introduction of hydroxy or phenylamino groups likewise causes an increase in activity. In general, the diarylamine type of age resister shows higher activity in the oxygen bomb than in the Geer oven. The tetraarylhydrazines (not reported here) are of extremely high activity. Diarylnitrosoamines and thiodiarylamines are of high activity, although for various reasons they are not widely used.

The specific properties of certain of the materials modify the generalizations made above. The effect of an age resister only slightly soluble in rubber is, of course, limited by the

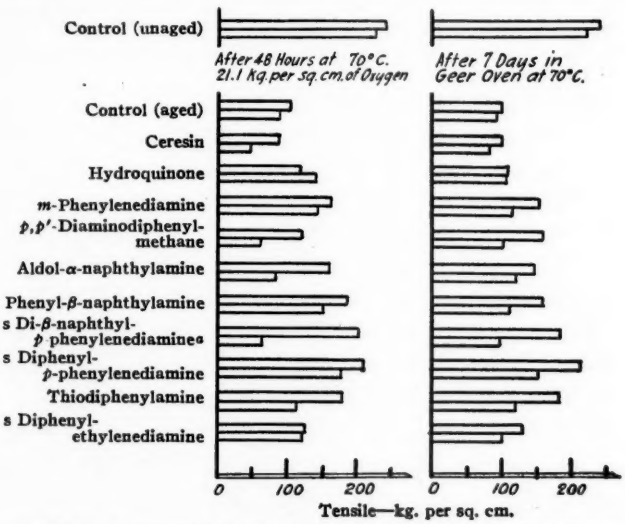

Figure 2—Comparison of Mill Incorporation and Surface Application of Various Materials for Retarding Deterioration of High-Grade Tread Stock

[a] See note under Figure 1.

amount which will dissolve. A surface bloom of age resister affords temporary surface protection but detracts from the appearance of the finished article.

Surface Application *vs.* Mill Incorporation

As shown on the charts, in nearly every case better protection was afforded by mill incorporation. The data indicate, however, that protection is not necessarily due to products formed during cure by reaction of the age resister with sulfur, rubber, resins, zinc oxide, or accelerator.

Results with Pure-Gum Stocks

In pure-gum stocks a similar order of activity of the age resisters obtained. However, the difference in effect between mill incorporation and surface application was small.

Tests for Inversion of Protective Action

Moureu (*8*) has cautioned that under slightly different circumstances "antioxygens may become proöxygens." In extensive work with the nitrogenous age resisters an inversion of their protective action has never been observed. With certain phenols variability of action has been secured when non-alkaline rubber compounds were used.

Table I shows the results of experiments in which 0.5 per cent of pyrogallol, aniline or their mutual salt was mill-mixed into the high zinc oxide, blooming tread stock previously mentioned. A comparison of the tensiles and especially the elongations after aging shows that pyrogallol has not retarded

Table II—Effect of Solvent Employed upon Accelerated Bomb Aging of Test Pieces Dipped for 10 Minutes in 5 Gram per 100 cc. Solutions of Phenyl-β-Naphthylamine

Stock Employed	
Selected pale crepe	100
Lithopone	100
Water floated whiting	75
Zinc oxide (lead-free)	5
Light mineral oil	5
Sulfur	3
Diphenylguanidine	1
	289

Cured in 2.4-mm. (3/32-inch) sheets in press 20 minutes at 142° C. (287° F.)

Solvent	Time in Bomb	After Aging in Bierer Bomb at 70° C. in 21.1 kg. per sq. cm. Oxygen		
		Ultimate tensile		Elong. at break
	Hours	*Kg. per sq. cm.*	*Lbs. per sq. in.*	%
Stock not treated	0	146	2075	523
	24	106	1514	500
	48	83	1184	435
	72	34	479	250
	96	Melted		
Acetone	0	146	2075	523
	24	148	2108	507
	48	138	1964	527
	72	125	1783	493
	96	122	1738	497
Alcohol	0	146	2075	523
	24	143	2034	500
	48	123	1753	537
	72	110	1558	530
	96	125	1770	505
Benzene	0	146	2075	523
	24	142	2022	505
	48	143	2027	520
	72	136	1934	517
	96	139	1940	510
For comparison, stock containing 0.5% phenyl-β-naphthylamine mill-mixed	0	155	2198	530
	24	147	2091	497
	48	147	2090	503
	72	118	1673	483
	96	130	1852	493

deterioration of the stock. The addition of aniline alone has slight preservative effect. The increased effect obtained by using pyrogallol and aniline in conjunction is apparent.

In general it has been found that certain acids or substances, which readily oxidize tend to accelerate deterioration. Sulfur, turpentine, and aldehydes may be cited as examples. The addition of organic basic materials more or less counteracts this effect and may even convert deterioration accelerators into deterioration retarders. Thus the addition of α-ethyl-β-

propylacrolein to a rubber stock accelerated with polybutyraldehyde aniline will cause it to soften and become very weak on aging. The further incorporation of an amine, such as aniline, metaphenylenediamine, or α-naphthylamine, will counteract the effect and impart superior aging properties to the stock.

Table II shows a comparison in which different solvents—acetone, alcohol, and benzene—were used as a means for applying phenyl-β-naphthylamine to a white stock. The parallel aging results show the small effect that inert solvents have upon deterioration. As one would expect, the benzene solution gave the best results and alcohol the poorest, since cured rubber is swollen appreciably by benzene and slightly by alcohol. The detrimental effects of a turpentine solution as noted by Moureu, Dufraisse, and Lotte (*10*) may be ascribed

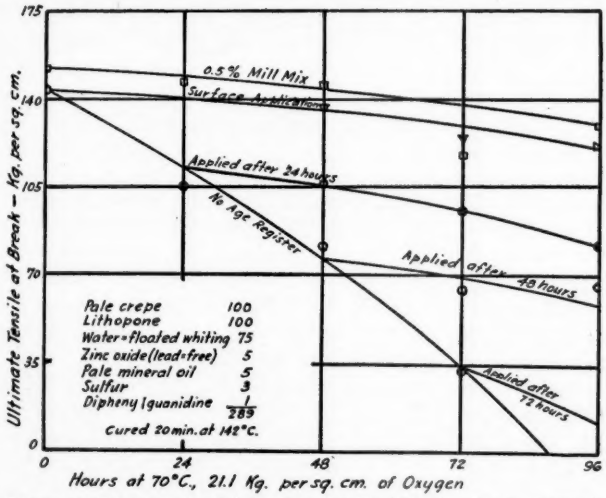

Figure 3—Effect of Applying Phenyl-β-Naphthylamine to Partially Aged Stock

to the well-known catalytic effect which autoxidizable materials exert in initiating the oxidation of rubber. One would also expect drying oils or aldehydes to be poor solvents for the application of age resisters to rubber even though the age resisters do retard the oxidation of these materials.

Retardation after Once Started

It was a point of general interest to determine whether the deterioration of rubber could be retarded after the action had once begun. The results of experiments designed to answer the question are represented graphically in Figure 3. Surface application of age resisters will inhibit deterioration even after it has progressed to a considerable extent. However, it would be better to guard against this need by the use of sufficient age resister in the compound prior to cure.

Limit of Protective Action

Age resisters do not exert their protective action indefinitely. In general high concentrations are more effective than low concentrations. This lends support to a theory that age resisters are consumed during the time that they exert their protective action, and does not fit in with a theory that the materials are being constantly regenerated.

Conclusions

If the results of bomb aging, oven aging, and sunlight exposure are compared, one is led to the conclusion that the deterioration of rubber is a complex phenomenon. The relative effectiveness of the different deterioration inhibitors varies with the test applied. The rubber technologist is interested, not only in the protection afforded against heat deterioration, continued cure, oxidation of the rubber, deterioration caused by oxidized sulfur, or deterioration induced by sunlight; but also in properties such as the activation of accelerators giving rise to definite desirable types of vulcanizates, plasticizing or stiffening of the uncured stock, improved dispersion of the pigments, decreased scorching tendencies, elimination of surface tackiness caused by dry air cure, and prevention of flexure cracking in the cured product. Surface application may be effective with respect to all of the properties listed in the first group, but only mill incorporation can lend the advantages enumerated in both groups. Moreover, wear will remove a large part of the age resister applied to the surface which cannot have penetrated by diffusion to a concentration beyond its solubility, whereas abrasive action may expose new portions of age resister milled into the stock.

Advantages of Mill Incorporation—(1) For high black stocks more effective protection is secured from mill incorporation than from surface application of age resisters.

(2) Larger amounts of preservatives in the compounds may be secured by mill incorporation, thus affording protection for a longer period of time.

(3) Owing to the slow diffusion into rubber of age resisters of high molecular weight, mill incorporation may be expected to give better protection to the interior of thick rubber articles than could be obtained by surface application. This holds true especially for protection against heat deterioration.

(4) It is evident that slightly soluble materials may be incorporated by mill mixing in amounts in excess of that needed to saturate the rubber, and as the dissolved part reacts and loses its effectiveness for protecting the rubber new portions of the excess may dissolve to sustain the protective action.

(5) Mill incorporation is much less laborious, since the material may be mixed into batches weighing 100 to 300 kg. (220 to 660 lbs.). Contrast with this the surface application to hundreds of single articles which might be produced from these batches.

(6) If the materials are incorporated on the mill, there is

no loss of costly solvent, with the attendant problems of recovery and of fire and health hazards.

ADVANTAGES OF SURFACE APPLICATION—(1) Surface application is the only means by which protection with age resisters can be secured for articles containing none, either new or after deterioration has commenced.

(2) Surface application is a means of applying materials which would materially interfere with the curing or processing of the stock.

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Early Stages of Oxidation in Rubber[1]

A Quantitative Application of the Pyrrole Test

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The pine splint–hydrochloric acid test for oxidation products of rubber has been developed in a quantitative way. The technic and special apparatus are fully described.

Data from application of the test to a wide range of commercial stocks are given. Its use in following early stages of oxidation as they occur in accelerated aging of vulcanized rubber is described, and attention is called to an apparent difference between oxygen aging and heat aging. Evidence is cited that the substance which gives the test, presumably levulinic aldehyde, is formed independently of, and previous to, the actual physical deterioration of the rubber.

BETWEEN rubber and the simple products of its ultimate oxidation many stages intervene. For the practical rubber technologist chief interest in this oxidative process is centered in that portion which has occurred up to the time when the rubber has so changed that it has lost its value as rubber.

This paper describes a semi-quantitative application of the well-known pine splint–hydrochloric acid test for pyrrole derivatives which the authors have found useful in following the early stages of oxidation in rubber, particularly in vulcanized rubber. It consists essentially of digesting the aged rubber with fused ammonium acetate, distilling with steam,

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and treating an ether extract of the distillate with an alcoholic pine-wood extract to which has been added hydrogen chloride. A red color develops, which is compared with a set of permanent standards.

Several different observers have noted that water will extract from oxidized rubber a substance which can be condensed with ammonium acetate, and thereupon gives the pyrrole color reaction with a pine splint. Bruni and Pelizzola (*2*) credit Gorter with being the first to record this fact, and cite several others who verified it. The active substance is generally assumed to be levulinic aldehyde, since the γ-ketoaldehydes give the reaction, and since Harries (*3*) and Whitby (*6*) have identified it among products from rubber ozonide and oxidized rubber, respectively.

Bruni and Pelizzola (*2*) simplified the test by heating the rubber directly with fused ammonium acetate and holding a pine splint in the vapors. They obtained positive tests with both raw and cured rubber which had been oxidized. It has been found possible, through a number of refinements, to increase greatly the sensitivity of the reaction, and to use the intensity of color developed as a comparative measure of the amount of this particular oxidation product in a sample. The sensitivity is such that it is usually possible to get positive tests before there is any evidence of physical deterioration as shown by tensile measurements.

Testing Technic

Figure 1 shows an apparatus which was developed for use in the test. With several of these in use simultaneously three or four analyses can be finished in from 20 to 30 minutes.

The rubber sample is cut into thin slices and accurately weighed. One gram is suitable for a stock only slightly aged, with smaller samples in proportion for those which are further advanced in oxidation. The sample is placed in the short-neck flask and from 2 to 3 grams of crystalline ammonium acetate are added. After the delivery tube has been placed in position, the flask is gently heated with a small direct flame until the acetate is completely fused, using care to avoid charring the rubber. Gentle heating is continued for from 3 to 5 minutes in such a way that the level of condensing vapors on the sides of the flask rises barely to the ground-glass fitting. After the flask has cooled, 8 to 10 cc. of water are added, and this is then distilled over into the long-stemmed flask as a receiver. Most of the ammonium acetate should remain in the distilling flask. The distillate in the receiver is diluted with water until it is about one-half way up the neck (it is convenient to make a mark on the neck of the flask indicating some definite volume). Two cubic centimeters of ether are added from a pipet. The flask is well shaken and two layers are allowed to form. The shaking and settling must be repeated several times

in order to complete the extraction. One-half cubic centimeter each of alcoholic pine-wood extract, alcoholic hydrogen chloride, and the above ethereal layer are then mixed in the order named in a small test tube. After standing from 5 to 10 minutes the mixture is compared for color with the previously made standards. Values are calculated for 1 gram of sample.

The pine-wood extract is made by extracting clean white-pine shavings in a Soxhlet apparatus for 16 hours. New shavings should be substituted about three times during the operation. The concentration of pine-wood extract seems to be unimportant provided an excess is present in the final determination. However, it has been found that water in the alcohol tends to decrease the sensitivity of the test and, although ordinary 95 per cent alcohol can be used successfully, better results are obtained if the alcohol is

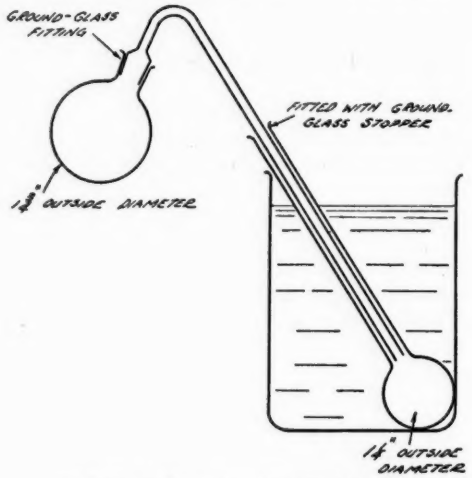

Figure 1—Apparatus for Pyrrole Test

practically anhydrous and solutions are protected from moisture of the air. The alcoholic hydrogen chloride is prepared by running dry hydrogen chloride into alcohol of the same composition as is used for the pine-wood extract, until it fumes strongly at the surface when exposed to the air. The two solutions must be kept separate until the test is made.

The accuracy of this method is not sufficiently great to demand the use of a colorimeter. For comparing colors small test tubes of about 1 cm. inside diameter have been used. Care was first taken to eliminate those of too large or too small diameter.

For standards of comparison some difficulties arose. It was originally intended to run through the test with a piece of badly aged rubber and use the resulting solution

and suitable dilutions of it as primary standards. The instability of the color, however, soon showed the impossibility of this, and the ultimate scheme was the use of water-soluble dyes in dilute buffered solutions of pH 7.0, and glass-sealed in the small test tubes mentioned above. Basic fuchsin, modified by traces of malachite green and auramine, gave a close approximation of the color actually obtained with aged rubber. A solution of this was given an arbitrary value of 10, and it was diluted down through a graded series to a lowest member with a value of 0.1. The color of this last member was a very faint pink. Standards thus prepared, and sealed in glass, have not changed appreciably in the course of a year's standing. Cork- or rubber-stoppered tubes are to be avoided, since the substances in the stopper tend to react with the dye.

Application to Typical Rubber Stocks

In Table I are listed some results with typical rubber stocks of various types and histories. It will be seen that there is an excellent qualitative correspondence between the pyrrole test and the amount of deterioration. The effect of antioxidant is strongly brought out both by the condition of the stock and by the magnitude of the pyrrole test.

In the used tire it is of interest that, even in the interior of the carcass as well as in the tread, there was definite evidence of oxidation. The acetone extracts of the carcass and tread were 8.2 and 13.8 per cent, respectively.

Table I—Comparison of Deterioration of Typical Rubber Stocks with Pyrrole Test

Type of Stock	Aging History	Anti-oxidant	Condition	Pyrrole Test
Thread	5 years shelf	No	Weak	1.8
		Yes	Very strong	0.2
White shoe upper	4 months sun + 5 years shelf	No	Weak, stiff	2.0
		Yes	Strong, pliable	0.4
Red shoe upper	5 years shelf	No	Strong	0.7
		Yes	Very strong	0.0
Inner tube	2 years weather	No	Weak	2.0
		Yes	Very strong	1.2
Carcass compound	4 months weather + 5 years shelf	No	Very weak	2.1
		Yes	Strong	0.2
Used tire carcass	3½ years service, 18,000 miles	No		0.7[a]
Used tire tread	3½ years service, 18,000 miles	No		0.8

[a] Tested without separation of fabric. On a rubber basis this figure should be at least twice as large.

Effect of Kind of Aging on Pyrrole Test

As a routine method for measuring deterioration, however, the pyrrole test can have only a limited application, since it will presently be shown that its relationship to physical properties is largely dependent upon aging conditions, which in natural aging may vary widely. The main use of the

test has been in trying to follow the actual process of oxidation, and the results have been most interesting and suggestive.

Table II gives data obtained with a simple rubber-sulfur (100 to 7 by weight) compound, which was calendered to 0.030-inch gage, and cured in open steam with a 30-minute rise and 130 minutes at 142° C. Three methods of aging were used—in oxygen at 21.1 kg. per sq. cm. and 60° C., in air at 70° C. (Geer oven), and also in air at 100° C.

Table II—Comparison of Physical Properties of a Stock and Pyrrole Test after Different Periods and Kinds of Aging

Time of Aging	Tensile Strength	Pyrrole Test	Acetone Extract
	Kg. per sq. cm.		*Per cent*
Unaged stock	143.4	0	5.1
Aged in oxygen bomb (hours):			
24	136.4	0.1	...
48	132.2	0.5	5.3
72	125.8	7.0	...
120	92.1	12.0	...
Aged in air at 70° C. (weeks):			
3 days	165.9	0.1	3.8
1	135.0	0.1	3.0
2	93.5	0.3	2.8
3	23.2	0.5	3.6
Aged in air at 100° C. (hours):			
4	129.0	0.2	...
8	85.8	0.3	...
16	57.6	0.4	...
24	8.2	0.7	...
36	4.4	0.7	...
48	4.4	0.6	...

From this table it can be seen that the pyrrole test indicates the beginning of the aging process at a much earlier stage than acetone extract data, and also that it is positive before there is any appreciable drop in tensile strength. The most interesting point, however, is that there seems to be a difference in character between aging in the oxygen bomb and in air at higher temperatures. In oxygen-bomb aging the pyrrole test continues to rise steadily throughout the course of aging. In heat aging the pyrrole test is positive after the shortest period employed, but rises only very slowly as aging progresses and seems to tend to a maximum which is very little larger than the first value obtained. Roughly, the figures in oxygen aging are from ten to fifty times as great as the corresponding stages of deterioration due to heat aging.

Comparison between the data in Tables I and II places the natural aging, as far as the pyrrole test is concerned, intermediate between the two types of accelerated aging. There is no evident quantitative agreement between physical condition and pyrrole test. This emphasizes the important distinction that the test cannot be regarded as one for rubber oxidation products in general, but is for a specific product or class of products—and, it is believed, a class which occurs early in the oxidative process. There is consequently no reason to expect any exact correspondence between the pyrrole test and the physical properties of naturally aged

rubber, since natural aging conditions can and do vary considerably, and some conditions may be expected to favor more than others the accumulation of a specific product.

Theory of Variation in Pyrrole Test

Bruni (*1*) failed to get any pyrrole test with stocks aged in a current of dry air at 77° C. and ascribed it to volatility of the product. Jones (*4*) apparently verified this conclusion by passing a slow stream of dry oxygen over heated rubber and condensing at the outlet a small amount of substance which gave the pyrrole test.

The present writers do not believe, however, that volatility of the product is the entire reason for the large differences noted in Table II. If such were the case it would seem to be entirely possible so to regulate the conditions as either to diminish or accentuate the volatility loss and to secure corresponding variations in the result. This was done, first by aging the sample in a "dead air pocket," which was simply a bottle entirely closed except for a section of capillary tubing piercing the stopper; and second by passing a continuous current of air over the sample. In both cases the temperature was 100° C. The results are given in Table III together with data for similar stocks aged in the oxygen bomb. Despite the difference in conditions the two heat-aged samples gave pyrrole tests of the same general magnitude and of a magnitude far below that of stocks aged under oxygen pressure. Furthermore, in the case of the sample aged in moving air no condensate was obtained which gave a pyrrole test, either in the conducting tubes or in a condenser immersed in ice.

Table III—Effect of Aging in "Dead" and Moving Air on Physical Properties and Pyrrole Test

Aging	Time	Tensile Strength	Pyrrole Test
	Hours	*Kg. per sq. cm.*	
Closed bottle at 100° C.	4	129.0	0.2
	24	8.2	0.7
Moving air at 100° C.	4	113.2	0.3
	22	15.5	0.4
21.1 kg. per sq. cm. oxygen pressure at 60° C.	72	125.8	7.0
	120	92.1	12.0

The writers believe that a better explanation of the difference in pyrrole test results lies in the hypothesis that levulinic aldehyde or similar material is formed comparatively early in the oxidation, without involving any great physical deterioration, and that in the subsequent course of actual physical deterioration it changes so that it no longer gives the pyrrole test. A tentative expression of such a hypothesis would be as follows:

$$\text{Rubber} \xrightarrow[\text{No physical deterioration}]{\text{Oxidation}} \text{(A) Positive to test}$$

$$\text{(A)} \xrightarrow[\text{Physical deterioration}]{\text{Heat}} \text{(B) Negative to test}$$

We might therefore expect that in the oxygen bomb, where conditions greatly favor oxidation, the first stage would proceed relatively faster, with an accumulation of early oxidation products. In heat aging the second part of the process might be favored, and the levulinic aldehyde destroyed almost as fast as it is formed.

The last data in this paper are centered around this hypothesis. If a fresh piece of the above-mentioned stock is aged at 100° C. in nitrogen from which oxygen has been very carefully excluded, the rate of deterioration is extremely slow and is presumably nothing more than a slow overcuring of the stock. If, however, before being put in the nitrogen it is placed in the oxygen bomb for a short period, the deterioration in nitrogen is much faster, even though it lost little or nothing in strength while in the oxygen bomb. In the actual experiment a piece was aged in the oxygen bomb for 72 hours without showing any drop in tensile strength, but it did show a decided pyrrole test. This piece was then placed in a tube filled with oxygen-free nitrogen and kept for periods of 24 and 72 hours, with the results noted in Table IV.

Table IV—Effect of Aging in Oxygen Bomb Previous to Nitrogen Aging

Blank Sample	Tensile after Aging at 100° C.	
	In air	In nitrogen
	Kg. per sq. cm.	*Kg. per sq. cm.*
Unaged	143.4	143.4
22 hours	8.2	136.7
7 days		112.5

Test Sample	Tensile	Pyrrole Test
	Kg. per sq. cm.	
72 hours in oxygen	148.3	1.4
Same plus 24 hours in nitrogen at 100° C.	73.1	1.0
Same plus 72 hours in nitrogen at 100° C.	32.3	0.6

It is seen that the test sample suffered a drop in tensile greater than might be expected solely from heating in nitrogen. That is, although the sample was as strong before the test as the blank itself, it nevertheless contained potentialities for deterioration which were not present in the blank. The writers think these potentialities are represented by the pyrrole test figures, and it may be noted that as the deterioration in nitrogen continued the pyrrole figures grew smaller. The experiment has since been repeated with essentially the same results. In this later experiment, in order to exclude oxygen which might remain dissolved in the rubber as a result of its having been in the oxygen bomb, the stock was subjected to a vacuum of 2 mm. for about 30 minutes before being placed in the tube containing nitrogen.

Conclusion

The foregoing will illustrate some of the applications which have been made with the test as developed by the

authors. Since the above work was completed, van Rossem and Dekker (*5*) have published their very significant paper on extraction of rubber with benzene–alcoholic potash mixture. Both methods apply to rubber at the same stage of its life, and it should be interesting to compare results from the same sample. In general it may seem that their method is of somewhat higher accuracy, while the pyrrole test requires less time and labor and is more informative as to the actual processes of oxidation.

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Laboratory Evaluation of Flex-Cracking Resistance[1]

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A machine has been designed for laboratory evaluation of the flex-cracking resistance of any stock from which a dumb-bell strip may be cut. The conditions under which the stock is tested may be varied at the will of the operator. The results obtained on this machine on tread and sidewall stocks have always evaluated the flex-cracking resistance of stocks in the same order that actual road tests have.

MANY factors are involved in the proper compounding of rubber stock. In tread compounding wear resistance is the major consideration, but other factors closely approach it in importance. Among these is the ability to withstand repeated flexing without cracking. Flex cracking produces an unsightly appearance which conveys the idea of inherent weakness in the tire, and also, if the flex cracking becomes very pronounced, the tire may fail from carcass break at that point. A satisfactory tire must not flex-crack.

Flex-cracking resistance is dependent on two things—the stock itself and the stress under which it is working. The design of the tire—that is, size and shape of the buttons, the size and position of the side ribs, and the amount of lettering on the side—regulates the working stress under which the sidewall and tread are operating. This accounts for the fact that two tires made by different companies may be different in flex-cracking resistance although of very similar or even identical compounding.

Various reasons have been advanced as to why one stock

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is better than another in regard to flexing resistance. A few of these reasons are: (1) better dispersion of the pigments, (2) better surface continuity, (3) fewer stock folds during forming and curing, and (4) better stress-strain properties. Arguments for and against these reasons have been advanced without any definite conclusion as yet.

Laboratory duplication of road-test conditions is the goal of all rubber technologists, as road testing is costly and time-consuming. A short study of the stresses under which the stocks in a tire work should tell us some things concerning what the laboratory machine for evaluating flex-cracking resistance should be like. A normally inflated tire is under less than 5 per cent elongation. If the tire were of uniform thickness and construction from bead to bead, the elongation

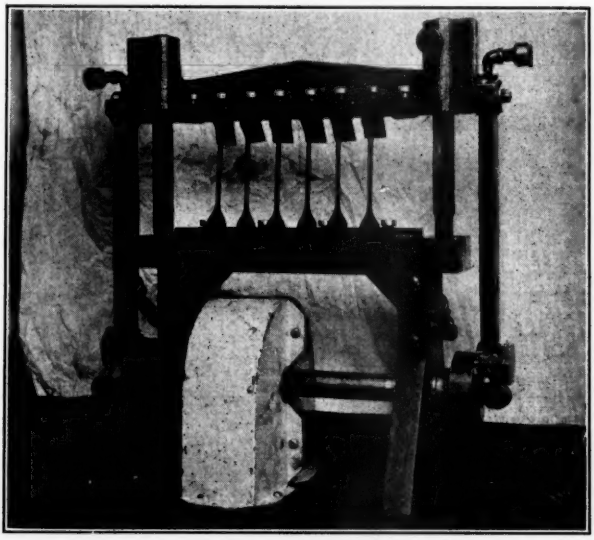


Figure 1—Apparatus for Evaluation of Flex-Cracking Resistance

would be uniform. However, such is not the case and therefore the tire has points of greater and lesser stress. As a result some part of the tread or sidewall may be subjected to an elongation of possibly 10 per cent as it makes a revolution under load. Some parts of the tire are under compression during road contact, but inasmuch as rubber is only as compressible as bronze (*1*) the movement is practically all elongation, and therefore flex cracking may be considered as the result of elongation. Therefore, a machine which subjects the rubber stock to repeated elongation should produce flex cracks.

Since the rigidity of a tire is due chiefly to the carcass fabric, the conditions under which the tread and sidewall operate are almost independent of the stress-strain properties of these

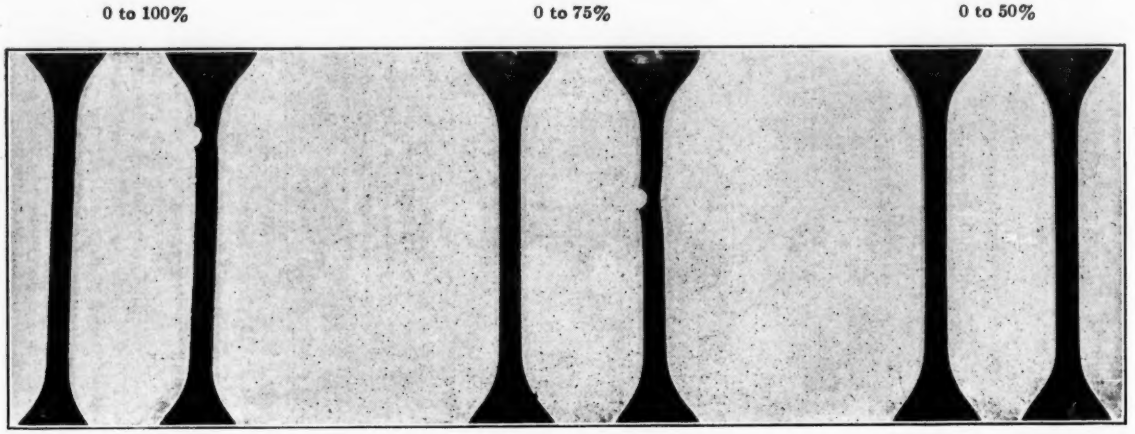
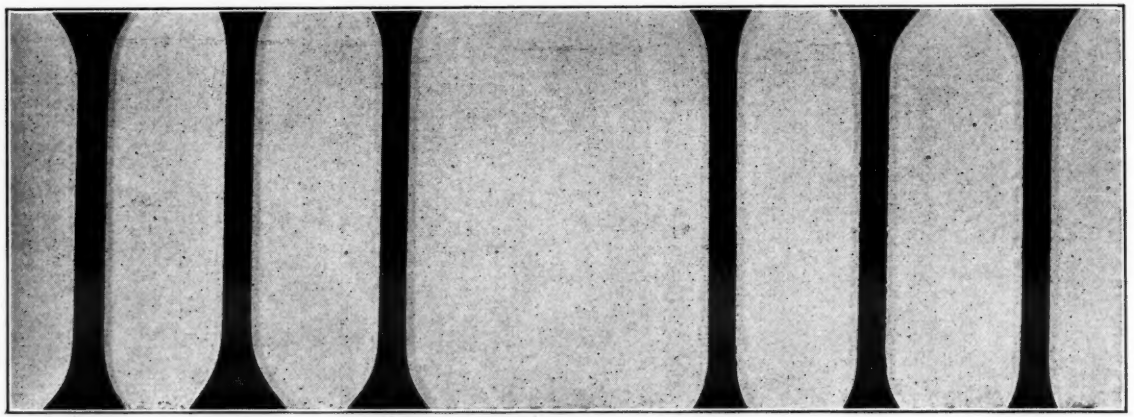


Figure 2—Effect of Varying Working Elongation

42½ lbs. of Black

50 lbs. of Black



Length of test, 2½ hours, elongation 0 to 100 per cent

Figure 3—Effect of Increased Pigmentation

two stocks. A laboratory evaluating machine should therefore work to a definite elongation and not to a definite load.

Ordinarily flex cracking does not become noticeable on road test, even in poor tires, until 4000 or more miles have been run. If the machine duplicated road conditions, one test would last 100 or more hours, or the equivalent of about 12 working days. The ideal machine would be one that could be set to duplicate road conditions and also one that could be so changed as to give accelerated tests.

Description and Operation of Testing Apparatus

For several years a machine for evaluating flex cracking has been in use in the Firestone laboratories. This machine

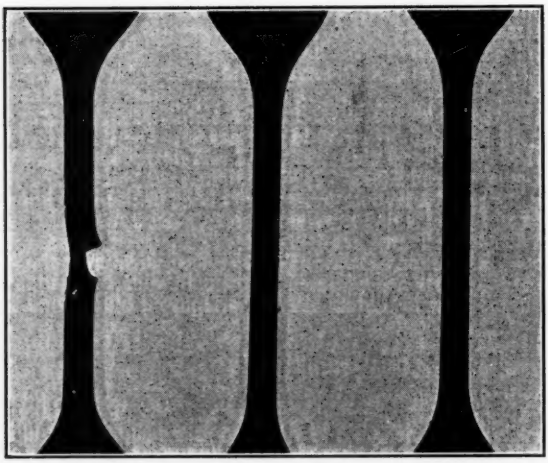


Figure 4—Effect of Adding Filler Pigment and Clay to Tread Stocks

has won the confidence of the organization because the results obtained with it and the results obtained by actual road test have always been in accord. This machine is illustrated in Figure 1. The test strip is the dumb-bell strip used in stress-strain testing, eight of which may be tested at one time on this machine. The upper beam oscillates vertically, and as the cams which actuate the driving arm and the sides of the upper beam are slotted, it is possible to obtain any initial setting between 1 and $4^1/_2$ inches and to vary the magnitude of the oscillation from practically 0 to 3 inches. The power is supplied by a $^1/_6$-horsepower motor. The pulleys are of such size that the upper beam oscillates about 400 times per minute.

The strips are fastened to the lower beam by means of a bar which is held down by four bolts with wing nuts. The

Control

1% Diphenylamine

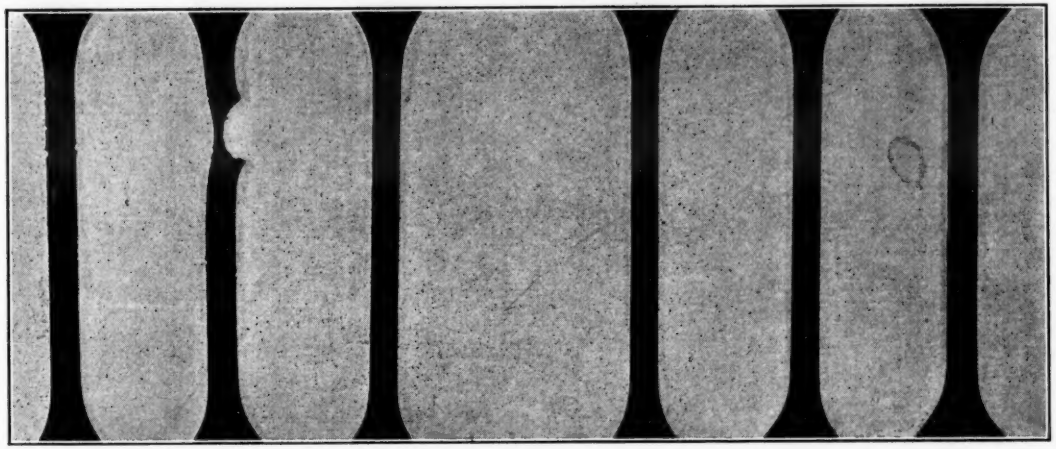


Figure 5—Effect of Adding 1 Per Cent Diphenylamine

upper beam is then set at the top of its stroke and each strip is individually secured to the top beam by means of a special screw clamp. These clamps are flattened eyelets and secure the strip by pulling it up into a slot in the upper beam. The slot in the upper beam is so tapered that strips of any thickness may be securely fastened. The strip is so placed in the upper beam that it is under maximum desired elongation. This elongation is measured in a manner similar to its measurement on a stress-strain machine. By adjusting the position of the driving arm in the cams at one end and in the upper beam at the other end, it is possible to subject the strip to any elongation desired.

Early experimental work with this machine established the fact that strips must be allowed to return to a position of 0 stress in each oscillation if any rapidity of checking is to be secured. After studying various conditions of test, the following procedure was adopted:

Minimum distance between beams	2¼ inches
Maximum distance between beams	5½ inches
Maximum elongation of the strip under test	100 per cent

Under these conditions it is possible to obtain flex cracks on the average present-day tread stock in about 8 hours with the machine making 400 flexes per minute, which is the number of flexes to which a tire in actual service is subjected when running 35 to 40 miles an hour. In running a test on a series of strips the test is continued only long enough definitely to rank the several stocks under test, and it is desirable, if possible, to stop the test before any strip actually breaks.

Effect of Varying Working Elongation

The effect of varying the working elongations under which the strip is flexed on this machine is shown in Figure 2. The stock used in this test was a tread stock containing 42½ pounds of channel black per 100 pounds of rubber; formula used is No. 1 in the accompanying table.

Formulas Used in Various Tests

Pigment	No. 1	No. 2	No. 3	No. 4	No. 5
Smoked sheet	100	100	100	100	100
Channel black	42½	50	42½	42½	42½
Zinc oxide	5	5	5	5	5
Sulfur	3	3	3	3	3
Stearic acid	3	3	3	3	3
Pine tar	4	4	4	4	4
Captax	1	1	1	1	1
Clay	...	...	40	...	...
Whole-tire reclaim	...	...	...	20	...
Diphenylamine	...	...	...	...	1

The strips on the left were subjected to 100 per cent elongation for 3 hours, at the end of which time they were loosened from the upper beam and allowed to hang free while the test was continued on the other four strips. After 6 hours the strips under a maximum elongation of 75 per cent were in a condition similar to those which were stressed at 100 per cent maximum elongation and loosened after 3 hours. The strips

which were flexed at only 50 per cent elongation were still in very good condition. To obtain flex cracks on the two strips shown at the right, it would have been necessary to run the test 10 to 12 hours longer.

Effect of Increased Pigmentation

Figure 3 shows the effect of increased pigmentation. The three strips at the left contain $42^1/_2$ pounds of channel black and are of the same stock used in the preceding test. The three strips at the right are identical, except that 50 pounds of channel black to 100 pounds of rubber were used (Formula 2). The detrimental effect of the increased pigmentation is very evident, and this is one of the reasons why more carbon black on the rubber is not used commercially.

Effect of Adding Filler Pigment and Reclaim

The results of the third test (Figure 4) illustrate the effect of adding to a tread stock filler pigment and reclaim, respectively. At present quotations whole-tire reclaim and the better grades of clay are about identical in cost on a volume basis. Although clay costs less than reclaim on a pound basis, the gravity of this material is twice that of whole-tire reclaim. Formula 1 was again taken as the basis of the test, and the strip on the left is the compound to which 40 pounds of clay have been added. The middle strip is from a compound made up by adding 20 pounds of whole-tire reclaim to Formula 1 (Nos. 3 and 4 in table). The volume costs on compounds 3 and 4 are identical and are about 10 per cent cheaper than that of the control, Formula 1. After 1 hour of flexing the clay stock was in very poor condition and was loosened from the upper beam, and the test continued on the other two stocks. After 2 hours the stock containing the reclaim began to show serious checking, and so the test was stopped. The control stock on the right showed only a very few minor checks.

Effect of Adding Diphenylamine to Stock

Figure 5 shows the effect on flex checking of adding 1 per cent diphenylamine to the control stock. The new formula is Formula 5. The beneficial effect of this amine is outstanding and would be of considerable commercial importance, except for the fact that other materials are available on the market which have the same property and other desirable properties as well. Among these materials are many of the antioxidants.

Comparison with Other Flex-Testing Machines

Several other flex-testing machines have been designed, and one which is highly regarded is the so-called India machine (*2*). This machine consists of a rotating disk inside of an off-center ring. In the rotating disk are cut radial slots in which specially cured test samples are inserted. As the disk

rotates the free end of each test strip is bent down so that its plane is at approximately a 90-degree angle to the plane of that part of the strip which is secured in the radial slot.

In comparing the two machines, several desirable features are evident in the Firestone machine. With this machine it is possible to evaluate the flex-checking resistance of any stock from which a dumb-bell strip may be cut. This makes the machine valuable to compounders who are working with stocks that are air-cured. The conditions of test may be varied so as to simulate any stressing condition desired. Furthermore, all types of stocks may be tested, as the resistance to abrasion of the stock does not enter into the test at all. The machine flexes the strips to a definite elongation and therefore the rigidity of the test strip in no wise affects the working elongation. Also, this machine can be mounted in the direct sunlight and run under conditions which are very comparable to actual road test, a feature which recent experience has shown to be highly desirable. Furthermore, the machine is small enough so that it can be encased and flexing determinations made at higher or lower than normal temperatures.

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Method for Preparing Micro-Sections of Rubber[1]

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IN THIS laboratory it is frequently necessary to prepare micro-sections of a large variety of rubber compounds, cured and uncured, containing from 2 to 50 volumes of pigment. Smear mounts are quite satisfactory for the identification of pigments, but not for dispersion investigations. There have been some indications that the pressure required to make the rubber thin enough to transmit light causes changes in the dispersion. Furthermore, rather high temperatures are required to cause the highly pigmented stocks to flow under the cover slip. Green's sulfur chloride method (*1*) of destroying the elasticity is unsatisfactory with uncured stocks, causes certain undesirable changes in the appearance of some stocks, and requires modifications in procedure with different types of compounds.

Freezing with liquid air has the inherent advantage that no permanent change is effected in the rubber and that all compounds, both raw and cured, can be treated essentially the same. Any of the usual mounting materials, however, such as paraffin wax, rosin combinations, etc., either crumble away, leaving little support for the rubber, or become so hard that the microtome knife is damaged.

The need for a mounting material which would overcome these difficulties brought wood into consideration. After experimenting with several kinds, basswood,[2] a soft wood with a straight grain and a uniform fibrous structure, was selected. Blocks 30 × 30 × 12 mm. (Figure 1-*A*) are cut and buffed flat and smooth on the surfaces to be in contact

[1] Received July 5, 1930.

[2] Only true basswood, especially *Tilia americana*, is suitable for this purpose. Wood from the tulip tree is sometimes incorrectly called basswood.

with the rubber. After a few coats of a thin rubber cement have been applied to these surfaces and allowed to dry, the specimen to be micro-sectioned, which should be about 8 × 2 × 0.5 mm., is placed between two of the blocks with its length at right angles to the grain of the wood, so that the sections will be cut parallel to the long fibers of the wood (Figure 1-*A*). The mount is then placed in a vise under pressure for several hours.

When the mount is removed from the vise it is carefully

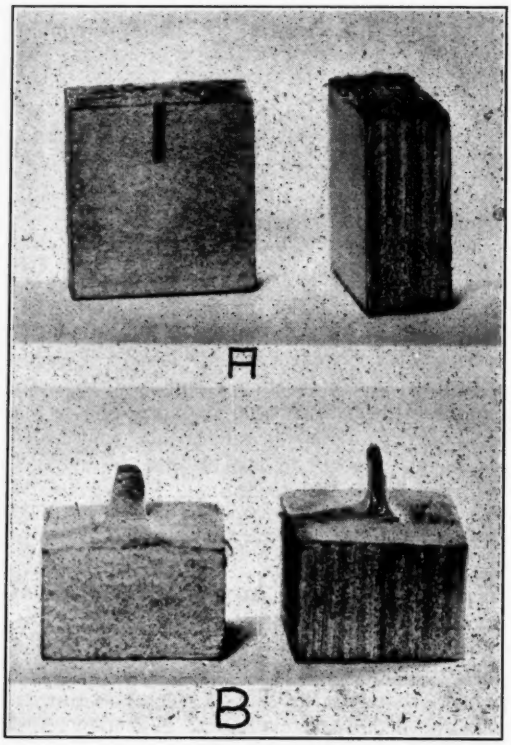

Figure 1—Basswood Mounting Blocks. Actual Size.

buffed on a grinding wheel, leaving a projection of wood holding the rubber (Figure 1-*B*). The block is then placed in the microtome clamp and liquid air applied with a $^3/_4$-inch paint brush. Liquid air is applied freely at first to prevent further contraction after cutting has been started. The mount has to be moved up 15 or 20 microns after the initial contraction due to the freezing, and liquid air should be applied frequently to prevent subsequent expansion. The microtome should be either hand-operated or of rapid short stroke. With such an instrument several micro-sections may be cut after each application of liquid air.

If permanent slide mounts are desired, it has been found best to use a dry knife and to select the best specimens under binoculars after they have been collected on a slide with a teaser. If the mount is not to be permanent, a few drops of glycerol on the knife collect the sections as they are cut. The glycerol carrying the sections is transferred from the knife to a slide with a glass rod and the cover slip applied.

For permanent mounting Aroclor 1257, made by the Federal Phosphorus Company, Birmingham, Ala., is very satisfactory. Its refractive index is about that of glass and its melting point is lower than most of the mounting media

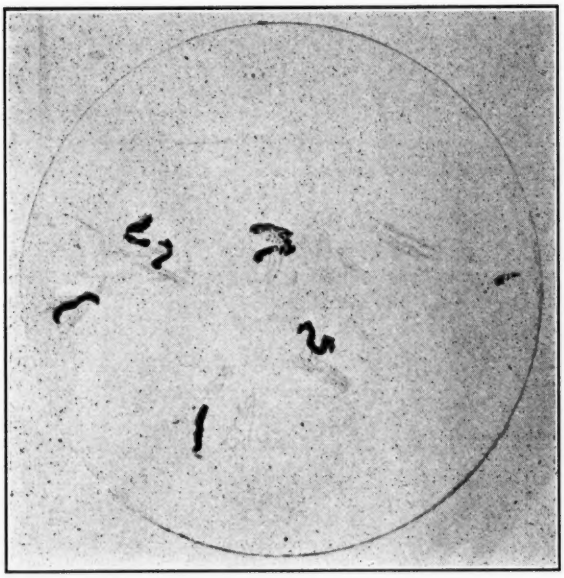

Figure 2—Finished Mount of a Five-Volume Carbon-Black Stock Showing Micro-Sections and Wood Fibers under Cover Slip. The Wood Fibers Are Very Faintly Visible. 4 ×.

otherwise suitable for rubber. While the slide is warm a gentle pressure on the cover slip usually causes the wood fibers to move away from the rubber which they have supported (Figure 2), giving an unobstructed view of the micro-section.

Owing to the tackiness of uncured stocks, they are more difficult to micro-section and great care must be exercised in handling them to secure satisfactory slide mounts. Excessively milled uncured compounds are too soft to be micro-sectioned. With this one exception the method as outlined has been found entirely satisfactory for micro-sectioning all types of rubber compounds, regardless of the amount of pigment or the state of cure.

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